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THE HYDPATES OF CHROMIUM CHLORIDE

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Two hydrates of chromium chloride are well known. In recent textbooks [1,2] mention is made of three hexahydrates differing in properties and in particular in their ability to react in aqueous solution with different amounts of silver ions. The respective structural formulas assigned to them are:

$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, $[Cr(H_2O)_6]Cl_3$.

(I) Green modification of Werner and Recoura (II) Green modification of Bjerrum (III) Grey modification

This mode of presentation is evidently borrowed from Werner's monograph [3]. Wyrouboff [4] claims the existence of a still larger number of isomers. Reports in the literature are conflicting. Werner and Gubser [5] suggest that the amount of precipitated chlorine depends on the duration and the conditions of precipitation. This is more clearly illustrated by Weinland and Koch [6]. On the other hand, Bjerrum [7], who believed that he had isolated an intermediate light-green chloride, neatly classifies them on the basis of analytical data as giving reactions for 1,2 and 3 chlorine atoms.

Gapon [8] used Bjerrum's scheme in an investigation of the kinetics of hydration of chromium chloride on the basis of stepwise separation of chlorine ions. This method is not reliable.

Determination of chlorine in the green chromium chloride hexahydrate by the volumetric method at room temperature gives results corresponding to the total chlorine content. The same results are also obtained in chlorine determinations at 0°. Chlorine determination by the gravimetric method gives variable results, depending on the temperature of precipitation and on the acidification up to the limit of the equivalent for the three atoms.

On following the instructions of Bjerrum, we failed to isolate his chloride, and its existence appears to us to be unproved both from preparative and thermographic standpoints (see below). Moreover, when the dark-green chloride is pulverized, it changes to light-green; the same change occurs when dried over sulfuric acid, and two molecules of water are lost. Bjerrum suggested that his product should be dried over sulfuric acid and in vacuum.

Karyakin [9] gave a recipe for the preparation of this chloride which led to the dark-green chloride of Recoura.

In one of his papers the latter [10] describes the preparation of a brown trihydrate of chromium chloride which is not an electrolyte and to which he assigns the formula: $[Cr(H_2O)_3Cl_3]$

Pfeiffer [11] also proposed Werner's structure for this product; he obtained this complex in aqueous solution but did not isolate it in the solid state.

In the opinion of these authors, therefore, chromium chloride formed a series similar to the series of Werner and Miolatti for cobalt and platinum.

On attempting to prepare Recoura's brown compound, we actually obtained (following his instructions) a change of color of the ethereal solution to brown and isolated a small amount of solid which we were inclined to regard as a product in which part of the water had been replaced by ether and which on contact with water was reconverted into the green modification. At all events, therefore, this brown modification is not as stable as the green or violet modification.

The electrical conductivity method was used for determination of the structure of the complexes. Werner had shown that whereas the molar electrical conductivity of the grey modification is constant from the very start (350 reciprocal ohms), the electrical conductivity of the green modification rises to the magnitude of the former in the course of several hours. This instability of the green modification, at least in weak concentrations, was not

clarified in the literature. Werner and Gubser [5] in one case in such solutions obtained an electrical conductivity of the order of 500 reciprocal ohms and did not give this fact the attention it deserved.

If we take into account the possibility of hydrolysis of the chloride to chromium hydroxide, then the molar electrical conductivity of such a solution may be expected to be of the order of 700 reciprocal ohms.

On measuring the electrical conductivity of 0.001 M solutions of chromium hydroxide, previously heated to 100° (i.e. solutions which may be strongly hydrolyzed), we obtained a molar electrical conductivity of the order of 680 reciprocal ohms.

In thermographic investigation of chromium chloride preparations with a straight thermocouple in an open vessel, the first halt is at 84°, corresponding to the melting point. Subsequently the temperature rises steadily and no halts are observed. This is evidently bound up with gradual loss of water. When the sample was heated in a vessel of the Stepanov type, i.e. under the pressure of its own vapor, apart from the melting point halt there was observed a halt at about 150°, corresponding to loss of water, and one at about 300°, marking the start of decomposition.

Thermograms obtained with a differential recorder on a Kurnakov pyrometer for the green modifications prepared by the method of Recoura and the method of Bjerrum (Figs. 1 and 2) were identical both in respect of the course of the curve and in that of the temperature halts on the curve. The first halt at 84° corresponds to the melting point of the sample; the second at 152° marks the complete removal of water.

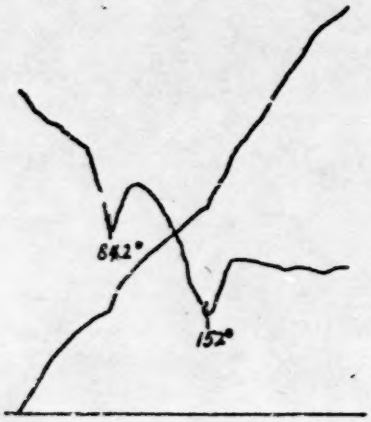

Fig. 1. Thermogram of Recoura's green chloride.

Fig. 2. Thermogram of Bjerrum's green chloride.

Fig. 3. Thermograms of the grey chloride.

Examination of the preparations by simple heating confirms the above observations.

When heated to 150-170°, all the water is lost, following which the weight remains constant. On heating to a higher temperature, there is observed - starting at 270-300° - a further loss in weight at the expense of chlorine; the green chloride at first then acquires a violet color; on further calcination it becomes dark-grey and then dirty-green. Chromium oxide is formed as a result of calcination. Rapid heating leads to cleavage of hydrogen chloride; slow heating results at first in loss of all the water and then in decomposition with loss of chlorine.

When moist samples are heated, yet another halt is observed on the thermogram, at 131.5°, corresponding evidently to loss of hygroscopic water.

The thermogram of the violet modification of chromium chloride hydrate gives two halts at 84 and 114° (Fig. 3).

From the structure of the isomers of the hexaaquo chromium chloride it was to be expected that, due to the different properties of the water located inside the sphere of the complex and that outside the sphere, the water would be lost at different temperatures. This was actually reflected on the thermogram.

X-ray powder diagrams, photographed at our request in a cylindrical camera of the Debye type using chromium radiation, showed identical X-ray patterns for the green modifications obtained by the methods of Recoura and Bjerrum. In both cases the X-ray diagrams were grainy. The picture is not substantially altered by grinding. These two diagrams are identical with the X-ray diagram of the anhydrous chloride which gives a normal

pattern. The X-ray diagram of the grey modification is less grainy than those of green modifications and differs slightly from the latter. The X-ray diagram of the anhydrous specimen contains a large number of lines.

The concept of the so-called hydrate isomerism, which finds mention in modern textbooks [1,3] mainly on the basis of chromium chloride, appears to us to be lacking a sound foundation. It is difficult to conceive that in the system water-dissolved salt for such a relatively simple case as chromium chloride hydrate, different forms could exist in solution for a longer or shorter period of time. Up to now too little consideration has been given to the difference between the state of a substance in the solid form and that in solution, especially in water.

SUMMARY

1. Of the four modifications of chromium chloride hydrate described in the literature, only two can reliably be said to exist - the grey (often described as violet in the literature) and the green modifications.

2. The method of argentometric analysis of [illegible] cannot be used as a method of distinguishing between the individual modifications.

3. Thermographic investigation did not reveal any difference between the two green modifications and between the behavior of the water in the inner and [illegible] sphere of a given modification.

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THE MECHANISM OF REDUCTION OF ACID SODIUM TUNGSTATES AND THE FORMATION OF BRONZES

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Researches of a series of authors [1,2,3,4] have established that whereas the electrolysis of fused neutral sodium tungstate leads to separation of metallic tungsten at the cathode, electrolysis of acid tungstates gives tungsten bronzes.

In the present research a study was made of the mechanism of reduction of acid tungstates by metallic sodium and of the conditions of formation of tungsten bronzes.

The mechanism of reduction of acid tungstates by hydrogen was studied by V. I. Spitsyn [5]. He showed that during the first stage of the process the acid tungstate loses an atom of oxygen to form the corresponding bronze. Later the reduction proceeds in the temperature interval of 550-700° in strictly consecutive order from a less reduced to a more reduced bronze with separation of the metal: blue bronze $-Na_2W_5O_{15}[Na_2O\cdot(WO_3)_4WO_2]$; violet bronze $-Na_2W_4O_{13}[Na_2O(WO_3)_3\cdot WO_2]$; red bronze $-Na_2W_3O_9[Na_2O(WO_3)_2\cdot WO_2]$; golden-yellow bronze $-Na_2W_2O_6[Na_2O\cdot WO_3\cdot WO_2]$.

The final product of reduction is neutral tungstate and metal.

Brunner [6] prepared bronzes by fusion of neutral or acid tungstate with tungsten dioxide in absence of air according to the equation:

$$Na_2WO_4 + WO_2 = Na_2W_2O_6;\ Na_2WO_4 + WO_3 + WO_2 = Na_2W_2O_8 \text{ etc.}$$

Philipp [7] obtained bronzes by reduction of acid tungstates with tin. He also showed that by fusion of bronzes with strongly acid or neutral tungstates it is possible to obtain bronzes respectively enriched or impoverished in tungsten trioxide. This method permits transition from one bronze to another.

Spitsyn and Cherepnev [8], when investigating the electrical conductivity of fused acid sodium tungstates, came to the conclusion that these compounds dissociate in melts with formation of free tungsten trioxide. A similar conclusion may be reached on inspecting the shape of the curve of the fusion diagram of the system sodium tungstate-tungsten trioxide.

It was previously shown that the first stage of the reaction of acid tungstates with sodium is marked by reduction of the free tungsten trioxide which is always present in the melt due to dissociation of the acid tungstate. Reduction of the trioxide proceeds according to the equations:

$$WO_3 + 6Na = 3Na_2O + W, \quad (1)$$

$$3Na_2O + 3WO_3 = 3Na_2WO_4, \quad (2)$$

or overall:

$$4WO_3 + 6Na = 3Na_2WO_4 + W. \quad (3)$$

Reaction (1) is a reaction of the eighth order and it is most unlikely that it takes place in one step. A more reasonable assumption is that reaction (1) proceeds through certain intermediate stages the first of which consists in reduction of tungsten trioxide to dioxide according to the equation:

$$2Na + WO_3 = Na_2O + WO_2. \quad (4)$$

Sodium oxide reacts further with excess of trioxide:

$$Na_2O + WO_3 = Na_2WO_4. \quad (5)$$

The over-all reaction of the first step of the process will proceed according to the equation:

$$2Na + 2WO_3 = Na_2WO_4 + WO_2. \quad (6)$$

In suitable conditions the formed tungsten dioxide is further reduced to tungsten. We might assume that the further reduction proceeds according to the equation:

$$4Na + WO_2 = 2Na_2O + W. \quad (7)$$

But this is a reaction of the fifth order, and its probability is likewise very low. Evidently the reduction of the dioxide to tungsten proceeds by another route.

Friderich and Sittig [9], when investigating the properties of lower oxides of some metals, established that calcination in vacuum of tungsten dioxide at 1500-1600° leads to decomposition into metallic tungsten and tungsten trioxide; the latter sublimed and was deposited on the cold part of the apparatus. On the other hand, when a pelleted mixture of the trioxide and metallic tungsten was calcined at 1000° in the absence of air, tungsten dioxide was obtained. The authors did not draw any conclusions whatever from these experiments. We may infer that a reversible reaction took place:

$$3WO_2 \rightleftarrows 2WO_3 + W. \qquad (8)$$

It is interesting to note that the thermal effect of this reaction, calculated from thermochemical data [10] at 18°, is 0.1 kcal, i.e. substantially equal to zero.

In normal conditions the equilibrium of reaction (8) is evidently shifted far to the left. If, however, the trioxide could be removed from the sphere of reaction, then the equilibrium would be shifted to the right and reaction (8) would proceed to completion with formation of tungsten. In the experiments of Friderich and Sittig, this was accomplished by using high temperatures (1500-1600°) at which the trioxide sublimed and left the sphere of reaction.

A similar case of an equilibrium shift occurs in the reaction of tungsten dioxide with hydrogen chloride. V. I. Spitsyn and L. I. Kashtanov [11] found that at 400° the following reaction takes place when a stream of dry HCl is passed over tungsten dioxide:

$$3WO_2 + 4HCl = 2WO_2Cl_2 + 2H_2O + W. \qquad (9)$$

Assuming that reaction (8) is valid and allowing for the volatility of tungsten oxychloride, we may propose the following scheme for reaction (9):

$$\begin{aligned} 3WO_2 &\longrightarrow 2WO_3 + W, \\ 2WO_3 + 4HCl &\longrightarrow 2WO_2Cl_2 + 2H_2O. \end{aligned} \qquad (9')$$

For the purpose of experimental verification of the possibility of displacement of the equilibrium of reaction (8), tungsten dioxide was heated in admixture with substances capable of combining with the trioxide formed in reaction (8), thereby shifting the equilibrium to the right. The substances selected had basic properties and were consequently able to combine with tungsten trioxide: sodium pyrophosphate, borax and calcium oxide. The tungsten dioxide required for the experiments was prepared by the method of van-Liempt [12] and C. A. Meerson [13].

Tungsten trioxide in a porcelain boat was reduced in a tube furnace at 850° for 3 hours with purified hydrogen which had been previously saturated with water vapor by passing it through two wash bottles containing water at 85-87°.

Reduction gave a brown powder of tungsten dioxide; the value of x in WO_x was calculated from the analytical data. We selected only those specimens of dioxide in which the value of x was not less than 2, since otherwise the dioxide would have been slightly over-reduced. A small under-reduction was of no consequence.

Sodium pyrophosphate, borax and calcium oxide were prepared in the pure form by the methods described in the literature.

Tungsten dioxide and one of the above-mentioned substances were mixed in a definite ratio and charged into a porcelain crucible; the crucible was placed in an iron bomb which was screwed tight with a cover, through an opening in which was led a porcelain tube for passage of a stream of dry, oxygen-free nitrogen.

The bomb, with crucible in position, was first carefully purged with nitrogen and then inserted in a furnace at red heat and kept there for an hour in a current of nitrogen. It was then cooled in a nitrogen stream. After an experiment the melt was lixiviated with water and the reaction products were collected and analyzed. Experimental results are set forth in Table 1.

All the three compounds gave pure metallic tungsten when heated with tungsten dioxide. The yield of tungsten was calculated from reaction (8).

Since none of the substances used is a reducing agent, the formation of metal can only be explained by reaction (8).

TABLE 1

Expt. No.	Added substance	Amount of added substance (in g)	Amount of WO_2 (g)	Molar ratio of added substance to WO_2	Analyzed comp. of WO_2	Reaction temp.	Comp. of obtained product	Yield of tungsten in % of theoretical	Yield of tungsten purity of W by analysis (in %)
1	Sodium pyrophosphate	22.0	3.45	5.17:1	$WO_{2.00}$	1000	Metallic tungsten	72.5	99.2
2	Borax	32.7	2.42	14.5:1	$WO_{2.02}$	920	Ditto	30.6	99.3
3	Calcium oxide . .	2.29	4.41	0.5:1	$WO_{2.06}$	930	"	35.0	99.9

The over-all reaction between the dioxide and the stated compounds may be represented by the following equations:

$$3WO_2 + 2Na_4P_2O_7 = 2Na_2WO_4 + 4NaPO_3 + W, \quad (10)$$

$$3WO_2 + 4Na_2B_4O_7 = 2Na_2WO_4 + 2(Na_2O \cdot 4B_2O_3) + W, \quad (11)$$

$$3WO_2 + 2CaO = 2CaWO_4 + W. \quad (12)$$

At the basis of reactions (10), (11) and (12) are the reactions:

$$Na_4P_2O_7 + WO_3 = Na_2WO_4 + 2NaPO_3,$$

$$2Na_2B_4O_7 + WO_3 = Na_2WO_4 + Na_2O \cdot 4B_2O_3,$$

$$CaO + WO_3 = CaWO_4,$$

of which the over-all expression is (8).

The results of the experiments are sufficiently convincing evidence of the occurrence of reaction (8).

Consequently the reduction of acid tungstates by metallic sodium may be considered to proceed in the following manner. The first stage in reduction of the acid tungstate is reduction of tungsten trioxide with formation of dioxide according to equations (4) and (5). The further course of the process depends on the state of equilibrium of reaction (8). The state of this equilibrium in the given conditions is determined by the properties of the medium. If the medium is basic, then the tungsten trioxide is bound and the equilibrium of (8) is shifted to the right in the direction of formation of metal. In an acid medium the equilibrium is shifted to the left and metal is not isolated.

When acid sodium tungstates are reduced, there will correspond to the basic or acidic character of the medium, respectively, an excess or deficiency of the sodium necessary for reduction of the whole of the free (excess) tungsten trioxide to metal. Let us consider this case more closely.

1. Excess of sodium. The reduction reaction proceeds in the following manner:

$$3WO_3 + 6Na = 3WO_2 + 3Na_2O,$$

$$3WO_2 = 2WO_3 + W,$$

$$2WO_3 + 2Na_2O = 2Na_2WO_4.$$

The residue of sodium oxide is bound by free trioxide.

$$Na_2O + WO_3 = Na_2WO_4$$

The sum of these reactions gives equation (3).

The reaction leads to separation of metallic tungsten.

2. Deficiency of sodium. There is an excess of tungsten trioxide in the medium. At the start, as in the preceding case, tungsten dioxide is formed, while sodium oxide is bound by excess of tungsten trioxide.

But due to the excess of trioxide, equation (8) will be shifted to the left. Hence the tungsten dioxide will not be decomposed with formation of tungsten, but dioxide will accumulate.

Tungsten dioxide is bound to form a bronze with sodium tungstate in accordance with Brunner's reaction:

$$Na_2WO_4 + WO_2 = Na_2W_2O_6 \quad (13)$$

and then, in presence of excess trioxide:

$$Na_2W_4O_{13} + WO_3 = Na_2W_5O_{16} \quad (14)$$
$$Na_2W_5O_{16} + WO_3 = Na_2W_6O_{19}. \quad (15)$$

Consequently, when acid tungstates are reduced with a deficiency of sodium, bronzes are certain to be formed and they are consequently products of incomplete reduction of acid tungstates.

V. I. Spitsyn showed that when acid tungstates are reduced with hydrogen the degree of reduction of the obtained bronzes increaseswith increasing amount of reducing agent. The bronzes may be arranged in the following order of increasing degree of reduction: Blue, violet, red, golden yellow. Similarly in reduction with sodium the degree of reduction must increase with increasing amount of sodium.

In our preceding paper we introduced the concept of the critical value of the sodium amount. By this term is to be understood the ratio (in %) of(on the one hand)the amount of sodium necessary for reduction of all the free trioxide to tungsten and neutral tungstate to (on the other) the amount of sodium necessary for complete reduction both of the trioxide and of all the neutral tungstate according to the equation:

$$Na_2WO_4 + 6Na = 4Na_2O + W$$
and $$WO_3 + 6Na = 3Na_2O + W.$$

If the amount of sodium used for reduction is less than the critical value, then an excess of trioxide remains and bronzes must be formed. Consequently the critical value may be regarded as a limiting value below which bronzes are obtained and above which tungsten is obtained.

The literature does not contain any data about the preparation of bronzes with the help of metallic sodium. It was therefore of interest to undertake a series of experiments on the reduction of acid tungstates by sodium. Reduction was accomplished in an iron bomb at 800-900°. After an experiment, the reaction mass was lixiviated with water and the character of the products was determined. The experimental results are set forth in Table 2. The amount of sodium (in %) was calculated in relation to the theoretical amount of sodium necessary for complete reduction of all the tungstate. In the sixth column are the critical values of sodium calculated for tungstate of the given composition.

The experimental results show that reduction of acid tungstates with an inadequate amount of sodium leads to tungsten dioxide and bronzes. The limiting character of the critical value of sodium is here very clearly illustrated. In all cases, when the amount of sodium even very slightly exceeds the critical value, metal is formed. If the amount of sodium is below this critical value, we obtain bronzes, tungsten dioxide or a mixture of these with metal.

When there is little tungsten trioxide in the starting mixture, reduction gives mainly dioxide. When there is a large proportion of trioxide we obtain bronzes. The closer the amount of sodium approaches to the critical value, the higher the degree of reduction and, conversely, with decreasing amount of sodium the degree of reduction correspondingly decreases. In this case we observe the same sequence as was established by V. I. Spitsyn for reduction of acid tungstates with hydrogen.

Such a sequence in the reduction of acid tungstates is fully explained by the above scheme. With an excess of trioxide the equilibrium of equation (8) is shifted in the direction of formation of dioxide which, as already shown, combines with tungstates to form bronzes in accordance with equations (13) to (15).

There is every reason for assuming that these reactions are reversible. Brunner showed that bronzes are capable of decomposing according to a reversible reaction, for example:

$$3Na_2W_2O_6 \rightleftarrows 3Na_2WO_4 + 2WO_3 + W.$$

But the last two terms of this equation are in equilibrium with WO_2 according to reaction (8).

On calculating the second equation from the first, we arrive at equation (13a) in analogy with equation (13):

$$3Na_2W_2O_6 \rightleftarrows 3Na_2WO_4 + 3WO_2. \quad (13a)$$

On the other hand, as already indicated above, we know from Philipp's work that bronzes are capable of enrichment or impoverishment in tungsten trioxide by fusing them with salts containing an excess or deficiency of trioxide. Consequently equations of the type of (14), (15), etc. are likewise reversible.

TABLE 2

Expt. No.	Composition	Amount (in g)	Amount of Na (% of the amt.)	Calc. val. of Na (%)	Reaction products
1	Eutectic: Na_2WO_4 80 mole-%, WO_2 20 mole %	22.2	2.[illegible]	5.0	Tungsten dioxide
2	Ditto	25.0	2.08	5.0	Tungsten dioxide
3	"	24.0	4.0	5.0	Mixture of tungsten dioxide and tungsten
4	"	14.6	5.2	5.0	Tungsten
5	"	25.0	6.3	5.0	Tungsten
6	Ditungstate $Na_2W_2O_7$	20.0	2.95	12.5	Mixture of tungsten dioxide and tungsten bronze
7	Ditto	20.0	6.2	12.5	Tungsten dioxide
8	"	15.0	12.7	12.5	Tungsten
9	Paratungstate $5Na_2O \cdot 12WO_3$	20.0	1.96	14.58	Mixture of red and violet bronzes
10	Ditto	20.0	4.2	14.58	Blue bronze (640°)
11	"	20.0	12.0	14.58	Golden-yellow bronze
12	"	25.0	17.6	14.58	Tungsten
13	"	20.0	26.5	14.58	Tungsten

On this basis we may conclude that reactions (8), (13), (14), (15), etc. form a group of closely linked reactions.

Decrease of Na →

$$2WO_2 + W \rightleftarrows 3WO_2 \quad (8)$$

$$Na_2WO_4 + WO_2 \rightleftarrows Na_2W_2O_6 \quad (13)$$

$$Na_2W_2O_6 + WO_2 \rightleftarrows Na_2W_3O_9 \quad (14)$$

$$Na_2W_3O_9 + WO_2 \rightleftarrows Na_2W_4O_{12} \quad (15)$$

← Increase of Na

With decreasing amount of sodium taken for the reduction the amount of residual trioxide increases and the equilibrium of all the above reactions will be shifted as the result downward, i.e. in the direction of formation of less reduced bronzes. With progressive increase of the sodium amount, the amount of residual trioxide will decline and the equilibrium of the whole group of reactions will be shifted to the left and upward. Hence we begin to get an increasing amount of dioxide — the last stage of reduction on the route to tungsten. As soon as the amount of sodium exceeds the critical amount, the latter stage of reduction will be attained and formation of tungsten will commence.

Consequently with gradual increase in the content of sodium and correspondingly gradual decrease in the quantity of trioxide, the reaction products pass successively through all the stages of reduction on the way to metal. The whole group of these reactions constitutes a unified complex in which each individual reaction is closely linked with all the others. This also accounts for the fact that usually we always obtain a mixture of bronzes, the separation of which into pure constituents is a rather complex problem when sufficient excess of trioxide is present.

SUMMARY

1. A study was made of the mechanism of reduction of acid sodium tungstates by metallic sodium. It was shown that this reaction proceeds in two stages. Tungsten dioxide is formed in the first stage. The second stage depends on the character of the medium and is governed by the state of equilibrium of the reversible reaction:

$$3WO_2 \rightleftarrows 2WO_3 + W.$$

2. It was established that when acid tungstates are reduced by sodium, the character of the reaction products depends on the degree of acidity of the medium. If the amount of sodium taken for the reduction is sufficient to impart a basic character to the medium, then the equilibrium of equation (8) will be shifted to the right, in the direction of formation of metallic tungsten. When there is a deficiency of sodium and the medium has an acidic reaction, then equation (8) is shifted to the left, in the direction of formation of tungsten dioxide.

sodium sulphates. The conditions of formation and the mechanism of formation of these salts were studied. It was also noted that the character of the curve depends on the activity of the components and is governed by the rate of equilibrium of a group of reversible reactions which are always linked with each other.

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RECIPROCAL SYSTEM OF THE DIAGONAL-BELT EUTECTIC TYPE OF METAPHOSPHATES AND SULFATES OF LITHIUM AND POTASSIUM

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The appearance of well-defined complexes in systems may completely alter the mechanism anticipated on the basis of the conventionally calculated stoichiometric effect of the exchange reaction [1]. The decisive factor governing the direction of a reaction is the ratio of the heats of the exchange reaction and of the complex-forming reaction. In systems containing one complex compound triangulation of three phase triangles may proceed in two diametrically opposed directions.

1) In the case of predominance of the heat of the reaction of exchange decomposition, the main triangular section is the diagonal (diagonal type: Fig. 1).

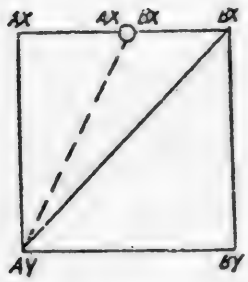
2) But when the heat of the complex-forming reaction predominates, triangulation is effected by a secant starting from the representative point of the double compound (diagonal type, in the triangulation of which none of the diagonals takes part; Fig. 2).

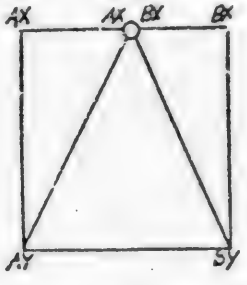
It appeared to be of very great interest to investigate systems containing well-defined complexes at opposite sides and a continuous series of solid solutions on the remaining two sides. We shall consider three types:

1) The reciprocal systems consist of three series of continuous solid solutions; the systems are divided into two tetragons with a single secant, [illegible] from both representative points of the compounds; the formed tetragons are not subjected to further triangulation (Fig. 3). Examples: Ca, Sr ‖ [illegible] [2]; Ba, Sr ‖ F, Cl [3].

2) The sharp displacement of the exchange decomposition causes a break in the continuous solid solutions and division of the stable diagonal into two phase triangles (Fig. 4). Example: K, Na | SO_4, F [4].

3) A special "belt" eutectic type is the reciprocal system (investigated by us) of the metaphosphates and sulfates of lithium and potassium Li, K ‖ SO_4, PO_3 (Figs. 5 and 13), described in detail in the concluding part of the paper. Its special characteristic is the presence in the system of a more stable section starting from the representative points of the complexes lying on opposite sides of the system. These sections of the system are divided into two tetragons which in turn are subjected to triangulation into two phase triangles. None of the diagonals in the triangulated system participates (Fig. 5). Neither the components nor the compounds form solid solutions with one another.





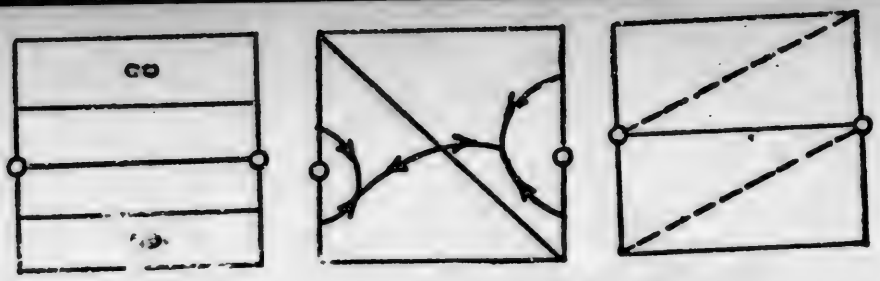
Figs. 1 and 2. Main types of diagonal systems with one complex component AX · BX on the sides.

EXPERIMENTAL

The investigation was carried out by the visual-polythermic method of fusion. The crucible was of platinum. The thermocouple was made of Pt—Pt/Rh alloy and incorporated an extremely sensitive multiscale millivoltmeter. The liquidus curves were determined from the temperatures of disappearance of crystals due to persistent vitrification of the melts enriched with lithium metaphosphate. Calculations were made with equimolar percentages. Lithium metaphosphate was prepared by fusion of chemically pure monoammonium phosphate with lithium carbonate. Melting points of salts: KPO_3 —798°; $LiPO_3$ —634°; Li_2SO_4 —860°; K_2SO_4 —1069°. Part of the tabulated experimental material has been omitted to cut down the length of this paper.

Binary Systems

1) $(KPO_3)_2$—K_2SO_4 (Table 1, Fig. 6). This system is here investigated for the first time. There is a eutectic at 22 % K_2SO_4 and 718°.



Figs. 3, 4 [illegible] types of reciprocal systems containing one complex compound at each of two opposing sides and a continuous series of solid solutions at the other opposing sides.

TABLE 1

% K_2SO_4	t°	% K_2SO_4	t°
2	790	43	820
4	782	45	852
6	776	50	874
10	766	54	888
13	758	60	908
16	752	64	926
20	736	70	941
21	728	75	961
23	728		
26	744		
30	764		
35	790		

TABLE 2

% $(LiPO_3)_2$	t°	% $(LiPO_3)_2$	t°
5	606	27.5	610
10	744	30	598
15	692	32.5	580
20	664	35	570
22.5	644		
25	628		

TABLE 3

% $(LiPO_3)_2$	t°	% $(LiPO_3)_2$	t°
4	774	36	536
8	744	40	544
12	720	42.5	551
16	694	50	562
20	666	55	550
24	641	60	532
28	609	65	528
32	582	70	548
		75	566

TABLE 4

% Li_2SO_4	t°	% Li_2SO_4	t°
3	774	45	564
6	747	50	576
9	720	55	582
13	682	60	578
16	647	65	574
20	612	70	554
23	590	75	539
25	574	78	520
27.5	568	82.5	524
30	564	85	540
33	562	90	569
36	550	92.5	620
40	530	95	700
41	540		

TABLE 5

% K_2SO_4	t°	% K_2SO_4	t°
26	538	[illegible]	[illegible]
27.5	528	[illegible]	605
29	520	[illegible]	6[illegible]3
30.5	504	58	[illegible]
32	[illegible]	[illegible]	620
33.5	460	[illegible]	642
35	470	68	666
36.5	478	[illegible]	69[illegible]
38	487	70	751
41	508	75	810
44	528	80	[illegible]
47	554		

TABLE 6

Section I [50% Li_2SO_4 + 50% K_2SO_4] → → $(KPO_3)_2$

% $(LiPO_3)_2$	t°	% $(KPO_3)_2$	t°
0	736	51	720
5	718	54	720
10	700	57	720
15	680	60	718
17.5	670	63	714
20	658	66	710
21	674	69	694
24	690	71	682
27	698	74	674
30	706	75	654
33	713	77	682
39	720	80	690
47.5	720		

2) Li_2SO_4—$(LiPO_3)_2$ (Table 2, Fig. 7). Investigated to 70% $(LiPO_3)_2$; further investigation hindered by viscosity. Eutectic at 47.5% $(LiPO_3)_2$ and 508°. Transformation point of the α-modification of Li_2SO_4 to the β-modification at 574° and 33.5% $(LiPO_3)_2$.

3) $(KPO_3)_2$—$(LiPO_3)_2$ (Table 3, Fig. 7). Investigated for the first time. A compound $LiK(PO_3)_2$ is formed at 562°. The eutectics correspond to: E_1—37% $(LiPO_3)_2$ and 528°; E_2—64% $(LiPO_3)_2$ [illegible]

TABLE 7

Section II
[50% Li_2SO_4 + 50% K_2SO_4] → → $Li_2(PO_3)_2$

% $(LiPO_3)_2$	t°	% $(LiPO_3)_2$	t°
0	736	40	554
5	710	45	534
10	690	50	506
15	670	52	494
20	648	54	493
25	624	55	505
30	604	57.5	520
35	580	60	530

TABLE 8

Section III
[50% $(KPO_3)_2$ + 50% $(LiPO_3)_2$] → → K_2SO_4

% K_2SO_4	t°	% K_2SO_4	t°
0	562	25	510
5	543	28	532
9	528	32	566
12	516	35	590
16	504	40	636
17.5	494	45	682
20	500	50	720
22.5	506		

TABLE 9

Section IV
[30% $(LiPO_3)_2$ + 70% Li_2SO_4] → → $(KPO_3)_2$

% $(KPO_3)_2$	t°	% $(KPO_3)_2$	t°
0	598	35	524
5	550	40	520
10	504	45	500
13	476	50	470
15	458	52	454
17	452	54	474
18	462	56	486
19	470	60	512
20	473	62.5	528
21	478	65	546
23	492	70	600
25	504	75	646
30	520		

TABLE 10

Section V [20% $(LiPO_3)_2$ + 80% Li_2SO_4] → $K_2(PO_3)_2$

% $(KPO_3)_2$	t°	% $(KPO_3)_2$	t°
0	664	45	540
3	606	50	520
5	564	55	508
10	538	56	500
13	510	57	490
15	482	60	512
17.5	467	62.5	526
20	484	65	536
25	528	70	540
30	550	75	600
35	550	80	660
40	548		

TABLE 11

Section VI [30% Li_2SO_4 + 10% K_2SO_4] → $(LiPO_3)_2$

% $(LiPO_3)_2$	t°	% $(LiPO_3)_2$	t°
20	566	46	496
25	552	48.3	520
30	538	51.7	534
33	530	55	554
36	524	58.9	566
39	508	64.8	582
42	496	72	601
45	484		

TABLE 12

Section VII [80% Li_2SO_4 + 20% K_2SO_4] → $Li_2(PO_3)_2$

% $(LiPO_3)_2$	t°	% $(LiPO_3)_2$	t°
0	539	45	491
5	530	48	504
10	524	51	520
20	510	54	536
25	502	57	545
30	494	60	560
33	487	63	572
36	478	66	582
39	476	69	591
42	470	72	600

TABLE 13

Section VIII [65% Li_2SO_4 + 35% K_2SO_4] → $Li_2(PO_3)_2$

% $(LiPO_3)_2$	t°	% $(LiPO_3)_2$	t°
0	674	35	494
10	642	37.5	480
15	617	40	462
20	586	43	460
25	558	45	484
30	528	50	500

TABLE 14

Section IX A [50% Li_2SO_4 + 50% K_2SO_4] → B [50% $(KPO_3)_2$ + 50% $(LiPO_3)_2$]

% B	t°	% B	t°
0	736	55	560
10	710	60	536
15	698	65	504
20	682	70	496
25	670	75	514
30	658	80	523
35	642	85	534
40	624	90	546
45	608	95	558
50	586	100	562

It was extremely interesting to observe a marked fall in viscosity of lithium metaphosphate under the action of the added potassium metaphosphate in spite of the formation of a double compound and a fall in melting point. The molecular structure of this compound is evidently less complex than that of lithium metaphosphate.

4) Li_2SO_4–K_2SO_4. Repeatedly investigated [5]. Forms a compound $Li_2SO_4 \cdot K_2SO_4$, melting, according to our determinations, at 736°.* Eutectics at: E_1 – 39% Li_2SO_4 and 712°; E_2 – 80% Li_2SO_4 and 535°.

* A. E. Bergman and E. K. Akopov later established the existence of the compound $2Li_2SO_4 \cdot K_2SO_4$, melting incongruently at 572°; consequently on the diagram of the reciprocal system from the 573° point of the lateral binary system the limit of the crystallization field is shown by a broken curve (Fig. 9). The field of this compound obviously terminates inside the system.

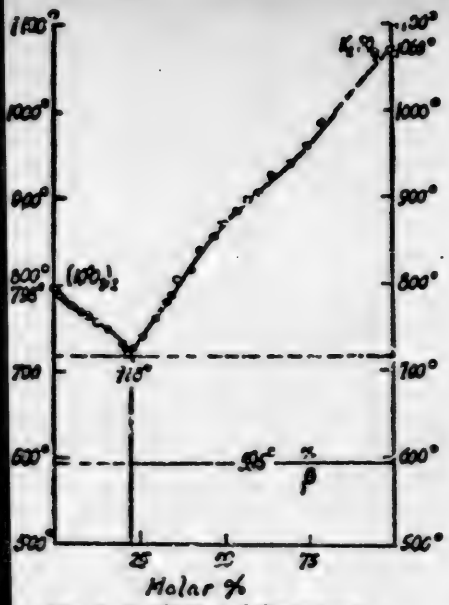


Fig. 6. Fusibility of the system $(KPO_3)_2$–K_2SO_4.

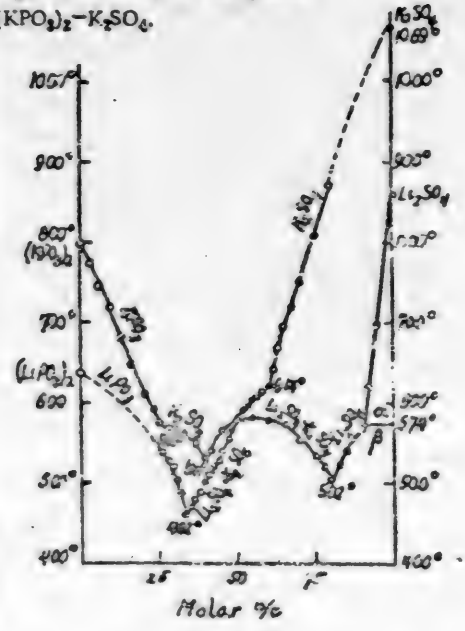


Fig. 8. Diagonal sections of the reciprocal system Li, K | SO_4, PO_3.

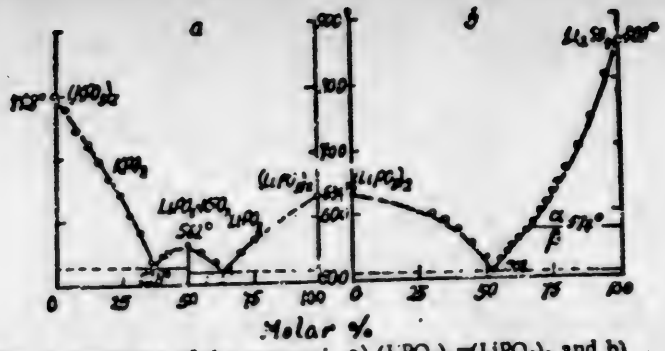


Fig. 7. Fusibility of the systems: a) $(KPO_3)_2$–$(LiPO_3)_2$ and b) $(LiPO_3)_2$–Li_2SO_4.

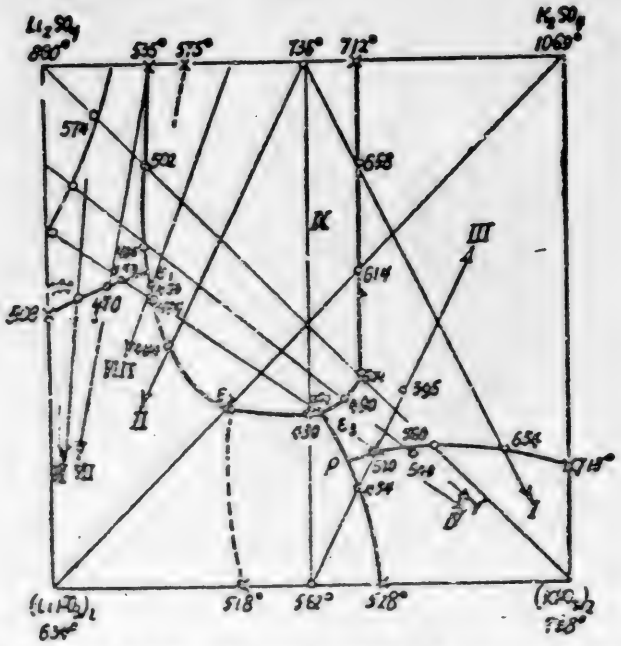


Fig. 9. Chart of internal sections through the reciprocal system Li, K | SO_4, PO_3.

Diagonal Sections

None of the diagonal sections is stable and both intersect the products of double decomposition.

1. $(KPO_3)_2$–Li_2SO_4 (Table 4, Fig. 8). The liquidus curve comprises branches of crystallization of potassium metaphosphate, the double sulfate of lithium and potassium, and the α- and β-modifications of lithium sulfate.

Points of intersection of the branches: 1) 26% Li_2SO_4 and 569°; 2) 40.5% Li_2SO_4 and 524°; 3) 55% Li_2SO_4 and 582°; 4) 80.5% Li_2SO_4 and 502°. Transformation points of the α- and β-modifications of Li_2SO_4 at 91% Li_2SO_4 and 574°.

2. Section $Li_2(PO_3)_2$–K_2SO_4 (Table 5, Fig. 8). The section intersects the field of crystallization of lithium metaphosphate, the double sulfate of lithium and potassium, and potassium sulfate. There is a slight inflection on the $Li_2SO_4 \cdot K_2SO_4$ branch at 50% K_2SO_4 whose significance we have not yet established.

Points of intersection of the branches: 1) 33% K_2SO_4 and 462°; 2) 60% K_2SO_4 and 614°.

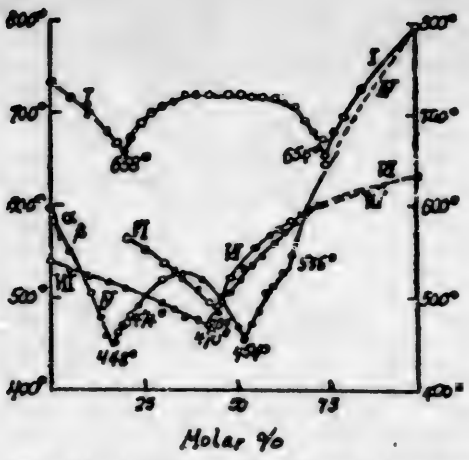


Fig. 10. Internal sections through the system:

I – 50% K_2SO_4 + 50% Li_2SO_4 → $[KPO_3]_2$;

VI – 90% Li_2SO_4 + 10% K_2SO_4 → $[LiPO_3]_2$;

IV – 30% $Li_2[PO_3]_2$ + 70% Li_2SO_4 → $[KPO_3]_2$;

VII – 80% Li_2SO_4 + 20% K_2SO_4 → $[LiPO_3]_2$.

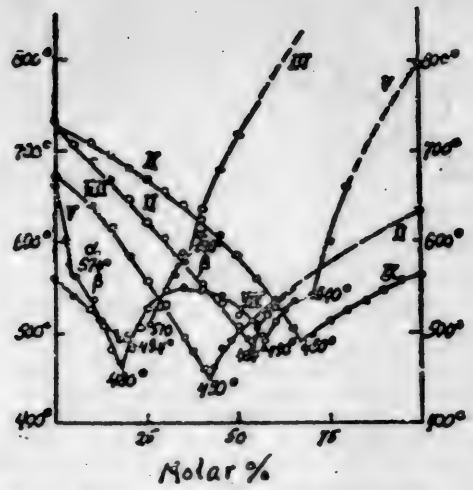


Fig. 11. Internal sections through the system:

II – 50% K_2SO_4 + 50% Li_2SO_4 → $[LiPO_3]_2$;

IX – 50% Li_2SO_4 + 50% K_2SO_4 → 50% $K_2[PO_3]_2$ + 50% $[LiPO_3]_2$

III – 50% $K_2[PO_3]_2$ + 50% $Li_2[PO_3]_2$ → K_2SO_4;

V – 20% $Li_2[PO_3]_2$ + 80% Li_2SO_4 → $[KPO_3]_2$;

VIII – 65% Li_2SO_4 + 35% K_2SO_4 → $[LiPO_3]_2$

Fig. 12. Spatial diagram of the reciprocal system Li, K ‖ SO_4, PO_3.

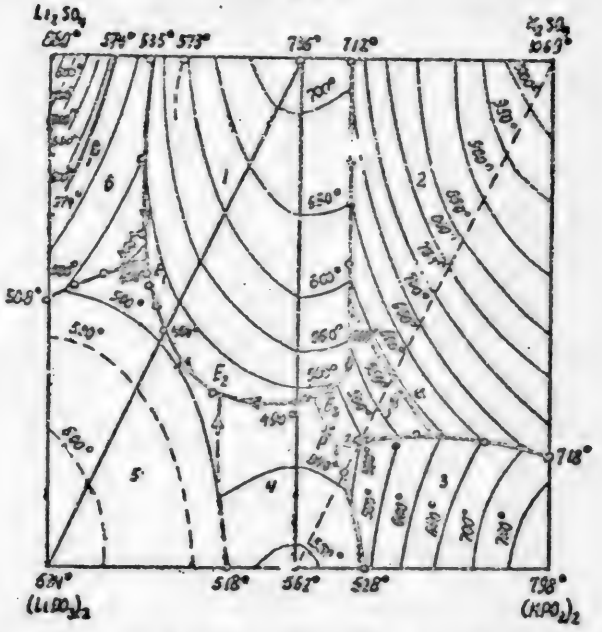


Fig. 13. Projection of the spatial diagram of the system on to the square of composition. 1) $Li_2SO_4 \cdot K_2SO_4$ field; 2) K_2SO_4 field; 3) KPO_3 field; 4) $LiPO_3 \cdot KPO_3$ field; 5) $LiPO_3$ field; 6) Li_2SO_4 field. E_1) 440°; E_2) 460°; E_3) 453; P) 474.

No. of field	Field of crystallization	Area (in %)	
1	Double sulfate of lithium and potassium		26
2	Potassium sulfate		30.6
	α-Modification of potassium sulfate	27.9	
	β-Modification of potassium sulfate	2.8	
3	Potassium metaphosphate		9.8
4	Double metaphosphate of lithium and potassium		7.9
5	Lithium metaphosphate		17.5
6	Lithium sulfate		8.3
	α-Modification of lithium sulfate	2.5	
	β-Modification of lithium sulfate	5.8	

TABLE 16

Type of point		Temperature	Composition (mole %)			Equilibrium phases
			Li_2SO_4	$(LiPO_3)_2$	$(KPO_3)_2$	
Eutectic	E_1	440	60	20.5	19.5	Li_2SO_4; $LiPO_3$; $Li_2SO_4 \cdot K_2SO_4$
	E_2	460	33.5	32.5	34	$LiPO_3$; $LiPO_3 \cdot KPO_3$; $Li_2SO_4 \cdot K_2SO_4$
	E_3	453	34	13	53	$LiPO_3 \cdot KPO_3$; K_2SO_4; $Li_2SO_4 \cdot K_2SO_4$
Transition P		474	24	19	57	$LiPO_3 \cdot KPO_3$; KPO_3; K_2SO_4

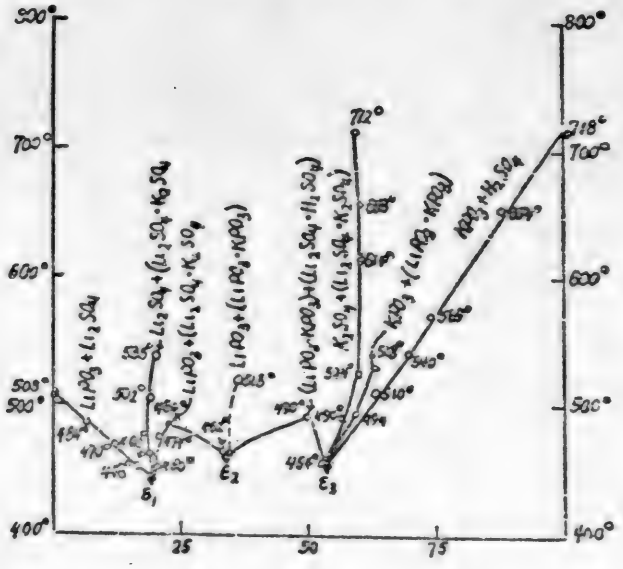


Fig. 14. Projection of the lines of common crystallization of the reciprocal system on to the side of $(LiPO_3)_2$—$(KPO_3)_2$.

Internal Sections Through the System (Fig. 9-11; Tables 6-14)

Section I. Points of intersection at: 1) 80% K_2SO_4 and 658°; 2) 75% K_2SO_4 and 654°.

Section II. Eutectic point at 54% $(LiPO_3)_2$ and 484°.

Section III. Points of intersection at: 1) 17.5% K_2SO_4 and 490°; 2) 25% K_2SO_4 and 510°. Transformation of α- and β-modifications of K_2SO_4 at 37% K_2SO_4 and 595°.

Section IV. Intersection points at: 1) 15% $(KPO_3)_2$ and 448°; 2) 21% $(KPO_3)_2$ and 474°; 3) 50% $(KPO_3)_2$ and 454°; 4) 64.5% $(KPO_3)_2$ and 536°.

Section V. Points of intersection at: 1) 12% $(KPO_3)_2$ and 460°; 2) 57% $(KPO_3)_2$ and 490°; 3) 70% $(KPO_3)_2$ and 540°. Transformation of α- and β-modifications of Li_2SO_4 at 4.5% $(KPO_3)_2$ and 574°.

Section VI. Point of intersection at 45% $(LiPO_3)_2$ and 470°.

Section VII. Point of intersection at 42% $(LiPO_3)_2$ and 470°.

Section VIII. Point of intersection at 42% $(LiPO_3)_2$ and 450°.

Section IX. Eutectic point at 67% $(LiPO_3)_2 \cdot (KPO_3)_2$ and 490°.

Spatial Diagram of the Reciprocal System (Figs. 12 and 13)

The isotherms in the lithium metaphosphate field are plotted with a broken line because here the field of vitrification was only partially investigated due to the experimental difficulty.

The projection of the curves of common crystallization on to the side of the square of the reciprocal system is represented in Fig. 14. The system contains three ternary eutectics and one ternary transition point (Table 16, Figs. 13 and 14).

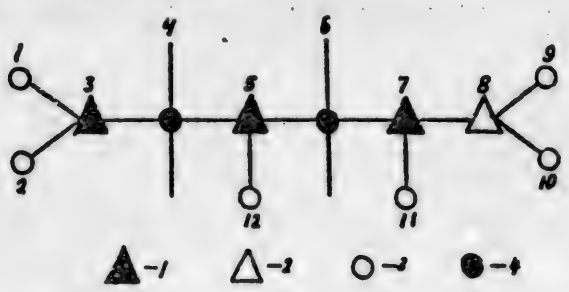


Fig. 15. Scheme of the crystallization field of the reciprocal system. 1) Ternary eutectic point (E_1, E_2, E_3); 2) ternary transition point (P); 3) binary eutectic point; 4) inflection point.

Sections II and IX are the sole stable sections of the system; they bear the character of simple binary systems whose eutectic points are turning points.

Section IX is the most stable*:

1) The fields of crystallization of the double sulfate of lithium and potassium are characterized by sharply defined ridges arranged along the given section.

2) The eutectic temperature of 490° of section IX is higher than the eutectic temperature (484°) of section II.

Fig. 15 is a diagram of the field of crystallization of the system: 1) 535°; 2) 508°; 3) 440°; 4) 484°; 5) 460°; 6) 490°; 7) 453°; 8) 474°; 9) 718°; 10) 528°; 11) 712°; 12) 518°.

Due to the absence of data for the heats of formation of $LiPO_3$ and KPO_3, it is impossible to calculate the arbitrary thermochemical effect of the double decomposition reaction; clearly it is very small, as could be determined from the fusion diagram. In both of the following equations the reaction between the starting components leads to formation of both of the double salts—of the components $Li_2SO_4 \cdot K_2SO_4$ and $LiPO_3 \cdot KPO_3$.

$$2Li_2SO_4 + 2(KPO_3)_2 \longrightarrow Li_2SO_4 \cdot K_2SO_4 + (LiPO_3)_2 \cdot (KPO_3)_2,$$

$$2(LiPO_3)_2 + K_2SO_4 \longrightarrow Li_2SO_4 \cdot K_2SO_4 + (LiPO_3)_2 \cdot (KPO_3)_2.$$

If the heat of the double decomposition reaction was higher than the heats of formation of the complexes, then reduction of both complexes should result in their decomposition with formation of a stable pair of components, as happens, for example, in the system Na, K || F, SO_4 [4]:

$$Na_2SO_4 \cdot NaF + 2K_2SO_4 \cdot KF \longrightarrow 3NaF + K_2SO_4,$$

in which the conventional thermochemical effect of the double decomposition reaction is 6.23 kcal per equivalent in the direction of the stable pair Na_2F_2—K_2SO_4.

Consequently the fields of both of the compounds $Na_2SO_4 \cdot NaF$ and $K_2SO_4 \cdot KF$ are separated from each other by the stable diagonal and by the fields of crystallizations of the stable pair of components. In the system that we have investigated, however, the fields of both of the complexes $Li_2SO_4 \cdot K_2SO_4$ and $LiPO_3 \cdot KPO_3$ diverge to form a transverse belt which separates the components capable of entering into exchange. The transverse section of $Li_2SO_4 \cdot K_2SO_4$—$Li_2(PO_3)_2 \cdot K_2(PO_3)_2$ divides the square into two tetragons which are subjected to secondary triangulation. The results of this investigation would be still more interesting if determinations were made of the heats of formation of metaphosphates of lithium and potassium and of the compound $LiPO_3 \cdot KPO_3$; the heat of formation of $Li_2SO_4 \cdot K_2SO_4$ has been determined [6].

SUMMARY

1. Using the visual-polythermic method of fusion, investigations were made of the liquidus surface of the binary systems

K_2SO_4—$K_2(PO_3)_2$; Li_2SO_4—$Li_2(PO_3)_2$; $K_2(PO_3)_2$—$Li_2(PO_3)_2$

and of the surface of crystallization of the reciprocal system Li, K || SO_4, PO_3.

* In Fig. 11 the stable sections are the dense, continuous curves; the unstable ones are indicated by broken curves.

2. The surface of crystallization of the reciprocal system consists of six fields, three ternary eutectics and one transition point.

3. The system is the simplest representative of a new diagonal-belt eutectic type.

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• See Consultants Bureau English Translation, p. 245.
•• See Consultants Bureau English Translation, p. 23.
••• See Consultants Bureau English Translation, p. 553.
•••• See Consultants Bureau English Translation, p. 2171.

CRYOSCOPIC INVESTIGATION OF THE SYSTEM NAPHTHALENE-IODINE-MERCURIC IODIDE. I.

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Formation of ternary systems is usually accompanied by solvation, complex-formation, association, or polymerization. These processes have attracted, and are still attracting, the attention of many investigators since they involve clarification of the properties of solutions (especially electrolytes).

In our investigation of the system naphthalene-iodine-mercuric iodide, we aimed at elucidating the effect of iodine on a solution of mercuric iodide in fused naphthalene. In our experimental conditions it was to be expected that this effect would be manifested in one of the two following directions: 1) the iodine would form complexes with HgI_2 (polyiodides); 2) the iodine would only facilitate association (or dissociation) of the mercuric iodide molecules.

The literature contains reports of the formation of polyiodides of various metals both in aqueous and nonaqueous solutions. KI with iodine in aqueous and alcoholic solutions forms the triiodide KI_3 [5]. A polyiodide of the same composition is formed when iodine and potassium iodide are dissolved in liquid SO_2 [1].

Plotnikov and others [2] investigated the electrical conductivity of iodides of the alkali metals in liquid iodine and arrived at the conclusion that the conductivity is caused by dissociation of polymers of polyiodides. Meyer [3] obtained polyiodides of the alkaline earth metals: BaI_4 SrI_4 CaI_4. Remy [4] observes (concerning polyiodides of the alkali metals): "... tetra-, and hexaiodides mainly of the heavy metals (Cu and Hg) also exist." Jorgensen [5] prepared mercuric hexaiodide HgI_6 in aqueous alcoholic solution. Polyiodides are only stable when a third component participates in their formation [6]. Polyiodides are not formed in solutions of mercuric iodide in liquid iodine [7].

The literature thus contains a series of statements about the formation of polyiodides of various metals, including polyiodides of mercury. In some cases iodine does not form polyiodides with a metallic iodide, notably with HgI_2.

EXPERIMENTAL

The naphthalene had m.p. 80.5°. The mercuric iodide was purified by solution in [illegible] alcohol followed by removal of the solvent. Iodine was sublimed and dried in a desiccator over KOH.

The melting points were determined in a Beckmann apparatus. A first series of experiments was performed in the following sequence: 1) The melting point of a weighed sample of pure naphthalene was determined; 2) to the naphthalene was added a weighed amount of iodine, and after solution in the fused naphthalene, the solidification point of the solution was determined; 3) to the iodine solution in naphthalene was added a weighed amount of HgI_2; after this had dissolved, the melting point was again determined. The difference between the melting point (Δt_1) of pure naphthalene and the melting point of the solution of iodine in naphthalene enabled calculation of the molecular weight of the iodine.

From the difference (Δt_2) between the temperatures of solidification of the solution of iodine in naphthalene and that of the same solution after addition of HgI_2, the molecular weight of mercuric iodide was calculated according to the formula:

$$M = \frac{K \cdot a \cdot 1000}{G \Delta t},$$

where K is the cryoscopic constant of naphthalene, 6.9; a is the weight of the substance whose molecular weight was determined; Δt is the depression of the solidification point of the solution; G is the weight of the solvent.

In a second series of experiments the order of addition of iodine and HgI_2 to the naphthalene was reversed: 1) mercuric iodide was first dissolved in naphthalene and the molecular weight was determined, 2) iodine was then

TABLE 1
First Series of Experiments.
Mol. wt. of I_2 - 254; mol. wt. of HgI_2 (calc'd. from the formula) = 454; weight of naphthalene 19.74 g

No. of prep.	Weight of iodine (g)	Millimoles in 1000 g naphthalene	Amt. of I_2 added to solvent (%)	Δt	Mol. wt. of iodine found	Wt. of HgI_2 (in g)	Millimoles HgI_2 in 1000 g solution	Δt	Mol. wt. HgI_2 found
1	0.2428	47.80	1.23	0.32	265	0.1166	12.93	0.06	679
2	0.1302	25.78	0.66	0.18	253	0.1166	12.93	0.06	679
3	0.0976	19.36	0.49	0.13	262	0.1166	12.93	0.06	679
4	0.0750	16.78	0.38	0.10	262	0.1166	12.93	0.06	679
5	0.0700	13.91	0.35	0.10	245	0.1166	12.93	0.06	679
6	0.0500	9.95	0.25	0.07	250	0.1166	12.93	0.06	679
7	0.0142	2.83	0.07	0.02	248	0.1579	17.60	0.08	690

TABLE 2
Second Series of Experiments

No. of prep.	Wt. of naphthalene (in g)	Wt. of HgI_2 (in g)	Millimoles HgI_2 in 1000 g naphthalene	Δt_1	Mol. wt. HgI_2 found	Wt. of iodine (in g)	Millimoles iodine in 1000 g solution	Δt_2	Mol. wt. iodine found
1	19.75	0.0800	8.93	0.07	399	—	—	—	
2	19.74	0.1166	12.93	0.10	407	—	—	—	
3	19.99	0.1180	12.92	0.10	407	0.2458	47.82	0.34	250
4	19.74	0.1166	12.93	0.10	407	0.2000	39.49	0.27	259
5	19.74	0.1366	15.13	0.11	434	0.0764	15.18	0.10	267
6	19.74	0.1166	12.93	0.10	407	0.0651	12.98	0.09	252

introduced and its molecular weight was determined. The results of this series of experiments are set forth in Table 2, where Δt_1 denotes the difference between the solidification temperatures of pure naphthalene and of the solutions of HgI_2 therein; Δt_2 is the difference between the temperatures of solidification of HgI_2 solution in naphthalene and of the same solution with addition of iodine.

EVALUATION OF RESULTS

The results of the cryoscopic investigation of the system naphthalene-iodine-mercuric iodide set forth in Table 1 show that, regardless of the amount of iodine previously added to the naphthalene, the molecular weight of the HgI_2 remains constant (679) and differs considerably from the molecular weight calculated according to the formula (454). Such a great exaltation of the molecular weight of HgI_2 in the conditions of our experiments may be explained either by formation of polyiodides or by association of molecules of HgI_2 in naphthalene solution. The ratio between the quantities of iodine and HgI_2 in our experiments varied over fairly wide limits: in the first experiment 3.7 moles iodine were taken for 1 mole HgI_2; in experiment 8 only 0.16 mole iodine was taken per mole HgI_2, i.e., an amount clearly insufficient for the formation of even a trijodide. If polyiodide had been formed in our experiments, then the varying amounts of iodine initially added to the naphthalene should have been reflected in the magnitude of the molecular weight of the compounds of iodine and mercury formed. The non-dependence of the magnitude of our determined value of the (apparent) molecular weight of HgI_2 on the amount of initially added iodine justifies the conclusion that polyiodides are not formed in our experiments. This conclusion is also supported by the results of the experiments set forth in Table 2. The molecular weight of HgI_2 is first (without previous addition of iodine) determined. In all cases it was close to 407 (a slight deviation only occurs in experiment 5), i.e., the molecular weight of HgI_2 determined in the absence of iodine was considerably below the calculated value (454). Such a ratio between the found and calculated molecular weights is a definite criterion that mercuric iodide dissolved in fused naphthalene undergoes dissociation.

In experiments 3, 4, 5, and 6 (Table 2), iodine was added to the solution of mercuric iodide in naphthalene, after which the molecular weight of the iodine was determined. In all cases the obtained molecular

iodine was close to the calculated value within the limits of experimental error. This justifies the following conclusions:

1) The iodine added to the solution of HgI_2 in naphthalene does not combine with the salt, i.e. polyiodides are not formed in this case.

2) The HgI_2 molecules do not undergo association after addition of iodine; in the event of their association the depression would not correspond to the calculated molecular weight of iodine.

Consequently, the second series of experiments also confirms our theory that HgI_2 and mercuric iodide do not form polyiodides in fused naphthalene. In such an event, the considerable elevation (679 instead of 454) of the molecular weight of HgI_2, established in the first series of experiments, can only be explained by association of the molecules of this salt, which would occur under the influence of the iodine previously added to the naphthalene. Without previous addition of iodine (expts. 1 and 2 in Table 2) no association of HgI_2 molecules is observed. Similarly, the addition of iodine after dissolution of HgI_2 in naphthalene (expts. 3-6, Table 2), does not bring about association of the molecules of this salt. The associating effect of iodine when introduced into naphthalene before dissolution of mercuric iodide in the latter and the absence of this effect when the iodine is added after dissolution of the HgI_2 may be explained in the following way. When HgI_2 is introduced into a solution of iodine in naphthalene, the molecules of this salt are first of all subjected to the action of the iodine in solution and they associate under the influence of the latter. It is possible that already associated molecules of mercuric iodide are then solvated. But when mercuric iodide is dissolved in pure naphthalene, its molecules are first of all subjected to solvation; the solvated molecules can no longer associate when iodine is added afterwards because the solvation shell formed round the HgI_2 molecules is a barrier to the action of the added iodine on them.

The degree of association of HgI_2 (according to Walden [1]) may be approximately calculated on the basis of the van't Hoff coefficient: $i = 454/679 = 0.67$; hence the degree of association $x = 1/i = 1/0.67 = 1.485$, or 1.5. Here x indicates how many times the found (apparent) molecular weight is greater than the calculated one (coefficient of association). The 1.5 times increase of molecular weight in our conditions may have the following very simple explanation: under the influence of iodine, the molecules of HgI_2 are associated into triple molecules of $(HgI_2)_3$ with a molecular weight of 1362. The associated molecules afterwards undergo electrolytic dissociation with complete breakdown into two ions, so that Δt is increased by a factor of 2, and the molecular weight is correspondingly halved, i.e., it becomes equal to 681 (in our experiments 679)*.

Plotnikov and co-workers [2] studied the electrical conductivity of solutions of iodides of a series of metals in liquid iodine or in $AlBr_3$ and came to the conclusion that the electrical conductivity is related to the association of the molecules of the dissolved substance. The iodides are only electrically conductive when their molecules are associated, i.e., only when the molecules of iodides undergo dissociation according to the scheme:

$$(MeI)_n \rightleftharpoons Me_nI^+_{n-m} + mI^-$$

Possibly a similar dissociation occurs of the molecules of mercuric iodide in our experimental conditions.

As we have already observed, more specific conclusions about all the processes taking place in the system naphthalene—I_2—HgI_2 necessitate a closer study of this system.

SUMMARY

The cryoscopic investigation of the system naphthalene—I—HgI_2 allows the following preliminary conclusions to be reached:

1) Polyiodides are not formed when iodine and mercuric iodide are dissolved in fused naphthalene.

2) The molecules of HgI_2 undergo association under the influence of iodine which has beforehand been added to the naphthalene.

3) Iodine does not bring about association of HgI_2 in solution in naphthalene if the iodine is added last

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* In our experiments the concentration of HgI_2, converted to $(HgI_2)_3$, was 0.004 mole. At such a concentration of the associated mercuric iodide, complete breakdown of its molecules into two ions may be considered probable.

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CRYOSCOPIC INVESTIGATION OF THE SYSTEM NAPHTHALENE-IODINE-MERCURIC CHLORIDE. II.

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In the investigation of nonaqueous solutions great attention is being paid —as previously noted by us [1]—to solvation and complex-formation. Sakhanov [2] explained the anomalous electrical conductivity of solutions from the standpoint of conductive complexes. Similarly Walden [3], in his numerous investigations in the field of nonaqueous solutions, explained the conductivity by polymerization and solvation of the dissolved substances. Electrical conductivity of solutions is usually explained by formation of complexes and solvates in them. An unanswered question, however, is to which of the cited processes in solutions should be attributed a high significance and to which a minor significance. This question is undoubtedly of fundamental importance for the theory of solutions. It would only be possible to establish the individual influence of each of the processes taking place in solutions on the properties of the latter if we were able to select and investigate systems in which the sole process taking place was either solvation or association or complex-formation. It is true that the two latter processes may proceed in solution side by side with solvation.

In our investigation of the system naphthalene-iodine-mercuric iodide [1] we established that association of HgI_2 molecules takes place under the influence of previously added iodine, but polyiodides are not formed. The I^- ions, of mercuric iodide, and the I_2 molecule, are mutually polarized. The increased magnitude of the dipole of HgI_2 due to the polarization facilitates association of these molecules. The Cl^- ion possesses a higher polarizing power than the I^- ion [4]; we may therefore suggest that $HgCl_2$ forms complexes with the strongly polarized I_2 molecules.

In this research we continue the elucidation of the problem of the influence of iodine on mercuric iodides with reference here to $HgCl_2$.

EXPERIMENTAL

The experimental procedure and apparatus have been described previously [1]. The reaction taking place in a solution of I and $HgCl_2$ in naphthalene proceeds slowly, and it is necessary to heat the solution at 81-85° for about 7 hours. In these circumstances, in all the experiments in this research the solution of mercuric chloride and iodine in naphthalene was kept at 81-85° for 7 hours before determination of the freezing point. The iodine color of the melt in all cases gradually became weaker during the heating period. A blank experiment in which iodine was heated in naphthalene (without $HgCl_2$) for 7 hours at 81-85° showed that in our experimental conditions the iodine substantially does not volatilize and the color of the melt remains unchanged.

In a first series of experiments the procedure was as follows: 1) Determination of solidifying point of naphthalene; 2) addition of weighed amount of mercuric chloride to weighed amount of naphthalene, determination of solidifying point and calculation of depression (Δt_1); 3) addition of weighed amount of iodine to solution of $HgCl_2$ in naphthalene, determination of solidifying point and fresh calculation of depression of solidifying point (Δt_2) (Table 1).

TABLE 1

Naphthalene Taken for Each Experiment 20 g

No. of expt.	Weight of $HgCl_2$ (in g)	Δt_1	Weight of iodine (in g)	Δt_2	Δt calculated	$\Delta t - \Delta t_2$	Amount of iodine taken (in g)	Millimoles iodine combined on basis of 1000 g naphthalene
1	0.1000	0.13	0.0220	0.02	0.03	0.01	0.007358	1.45
2	0.1000	0.13	0.0200	0.02	0.03	0.01	0.007358	1.45
3	0.1000	0.13	0.0468	0.05	0.06	0.01	0.007358	1.45
4	0.0500	0.07	0.0468	0.05	0.06	0.01	0.007358	1.45
5	0.1000	0.13	0.0514	0.04	0.07	0.03	0.0220	4.35
6	0.1000	0.13	0.0600	0.08	0.08	0	0.0590	11.81
7	0.1000	0.13	0.0900	0.09	0.12	0.08	0.05889	11.6

A second series of experiments was performed in the following order (Table 2): 1) Determination of solidifying point of naphthalene; 2) addition of weighed amount of iodine to weighed amount of naphthalene, determination of solidifying point and calculation of depression (Δt_1); 3) addition of weighed amount of mercuric chloride to solution of iodine in naphthalene, determination of solidifying point and calculation of depression Δt_2.

The last two columns of Table 1 contain the number of grams and millimoles of combined iodine; the fifth column of Table 2 contains the number of grams and millimoles of combined mercuric chloride. These values were obtained in the following manner.

TABLE 2

Naphthalene taken for all tests 20 g.

No. of expt.	Weight of iodine (in g)	Δt_1	Weight of $HgCl_2$ (in g)	Δt_2	Δt calculated	$\Delta t - \Delta t_2$	No. of grams of combined $HgCl_2$	Millimoles of $HgCl_2$ combined, on basis of 1000 g naphthalene
1	0.0440	0.06	0.1000	0.09	0.13	0.04	0.0315	5.8
2	0.0468	0.06	0.1000	0.10	0.13	0.03	0.0236	4.35
3	0.0508	0.07	0.1000	0.04	0.13	0.09	0.0710	13.07
4	0.0600	0.08	0.1000	0.05	0.13	0.08	0.0630	11.6
5	0.0882	0.12	0.1000	0.09	0.13	0.04	0.0315	5.8

That depression Δt, was calculated which would be caused by addition of a given weight of iodine (or $HgCl_2$), and from the difference $\Delta t - \Delta t_2$ was calculated the number of grams of combined iodine (or $HgCl_2$). The obtained amount of iodine (or $HgCl_2$) was recalculated on the basis of the content in 1000 g naphthalene and expressed in millimoles.

EVALUATION OF RESULTS

We see from Table 1 that: 1) With an iodine quantity of 0.0220 to 0.0468 g and a $HgCl_2$ weight of 0.1000 g, the latter combines with 1.45 millimoles of iodine (converted to 1000 g naphthalene).

2) With an iodine weight of 0.0514 g to 0.0838 g and an $HgCl_2$ weight of 0.1000 g, the amount of iodine combined is 4.35 to 11.6 millimoles; this amount is the maximum that can be bound by 0.1000 g mercuric chloride, since from 0.0600 g iodine (expt. 6) and from 0.0800 g iodine one and the same amount of it is bound.

3) In experiments 5-7 the number of millimoles of bound iodine is a multiple of 1.45; this regularity permits the conclusion that in all the above cases definite compounds of iodine with mercuric chloride are formed.

4) In experiments 3 and 4, with identical amounts of iodine (0.0468 g) and different amounts of $HgCl_2$, the number of millimoles of combined iodine is the same. Evidently 1.45 millimoles is the minimum amount of iodine that can be bound by 0.0500 g $HgCl_2$.

The following facts emerge from an evaluation of the second series of experiments (Table 2).

1) The number of millimoles of combined mercuric chloride in all the experiments is a multiple of 1.45. This regularity, like that noted for the first series of experiments, is undoubtedly also evidence that iodine and mercuric chloride form definite chemical compounds.

2) In connection with experiments 1 and 5, in each case 5.8 moles $HgCl_2$ are bound. The mystery is explained by comparing the amounts of iodine combined with these amounts of $HgCl_2$. As we saw from the first series of experiments, with iodine amounts in the range of 0.0220 to 0.0468 g the amount combined is 1.45 millimoles, while in the range of 0.0600 to 0.0838 g the amount combined is 11.6 millimoles. We can therefore conclude that in the first experiment (Table 2), out of 0.0440 g iodine, 1.45 moles is bound, while in expt. 5 out of 0.0882 g 11.6 millimoles are bound, i.e., in the case of the larger amount of iodine one and the same amount of $HgCl_2$ combined with more iodine.

3) Taking from Tables 1 and 2 those experiments in which the amounts of iodine dissolved in naphthalene are either identical or very similar and comparing them with the amounts of combined $HgCl_2$ (Table 2), we can see that iodine and $HgCl_2$ form complex compounds in fused naphthalene. These comparisons are shown in Table 3.

Comparison of the results in Tables 1 and 2 gives an indication of the composition of the complex.

TABLE 3

Weight of iodine (in g)		Weight of $HgCl_2$ (in g)		Ratio of millimoles of combined $HgCl_2$ and I_2	Formula of complex compounds
Number of experiment					
2nd series	1st series	2nd series	1st series		
1	3	1	3		
0.0440	0.0468	0.1000	0.1000	5.8 : 1.45 = 4	$4HgCl_2 \cdot I_2$
2	4	2	4		
0.0468	0.0468	0.1000	0.0500	4.35 : 1.45 = 3	$3HgCl_2 \cdot I_2$
2	4	2	3		
0.0468	0.0468	0.1000	0.1000	4.35 : 1.45 = 3	$3HgCl_2 \cdot I_2$
3	5	3	5		
0.0508	0.0514	0.1000	0.1000	13.07 : 4.35 = 3	$3HgCl_2 \cdot I_2$
4	6	4	6		
0.0600	0.0600	0.1000	0.1000	11.6 : 11.8 = 1	$HgCl_2 \cdot I_2$
5	7	5	8		
0.0882	0.0900	0.1000	0.1000	5.8 : 11.6 = 0.5	$HgCl_2 \cdot 2I_2$

On comparing the results of our investigations of the systems naphthalene–I_2–HgI_2 [1] and naphthalene–I_2–$HgCl_2$, we arrive at the conclusion that the effect of iodine on HgI_2 dissolved in fused naphthalene differs from the effect on $HgCl_2$. In the former system the only effect of the iodine is to cause association of HgI_2; in the second system complexes of iodine with molecules of $HgCl_2$ are formed.

SUMMARY

1. Cryoscopic investigation of the system naphthalene–iodine–mercuric chloride permits the conclusion that $HgCl_2$ with iodine forms complexes, polyhalides.

2. The probable formulas of these polyhalides were found to be: 1) $4HgCl_2 \cdot I_2$; 2) $3HgCl_2 \cdot I_2$, 3) $HgCl_2 \cdot I_2$ and 4) $HgCl_2 \cdot 2I_2$.

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*See Consultants Bureau English Translation, page 1189.

SOLUBILITY IN THE SYSTEM KSCN – K_2SO_4 – H_2O

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We carried out an investigation of the equilibria in the system KSCN–K_2SO_4–H_2O at 25 and 40° for the purpose of obtaining experimental data for the joint solubility in water of two salts with a common cation and markedly differing from each other in respect to their individual solubilities and to the structures of their anions. This investigation is a continuation of research by one of us on the effect of unlike anions of differing structures on the change of individual solubilities of the salts in ternary solutions of aqueous-salt systems with a common cation [1].

The system KSCN–K_2SO_4–H_2O has not been studied completely, as far as could be judged from the literature. We studied this sytem at the above-mentioned temperatures by the well-known isothermal method. The composition of the liquid phase was determined on the basis of quantitative determinations of SCN^- and SO_4^{2-}. The composition of the solid phase present in equilibrium with the solution was established by observations under the microscope of the external appearance of the crystals of the solid. The solid phases for the univariant curves of the isotherms are the individual salts, while those for the eutectic points are mixtures of salts.

It should be noted that the period necessary for attainment of the equilibrium state in the system KSCN–K_2SO_4–H_2O increased with rising concentration of KSCN in the liquid phases: at KSCN concentrations of 45% by weight and higher, the equilibrium was established after 24-30 hours.

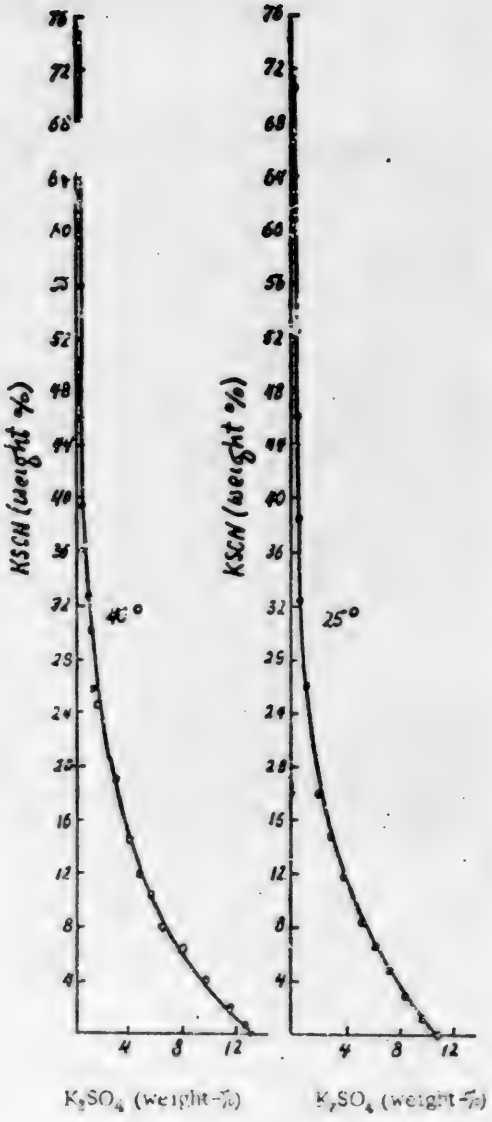
The experimental material for the system KSCN–K_2SO_4–H_2O is set forth in the table and graphically represented in the diagram. From the diagram we see that the branches of crystallization of K_2SO_4 in both of the isotherms determine the character of the equilibria in the system, whereas the branches of crystallization of KSCN (barely visible on the diagram) are entirely without significance since the solubilities of this salt in the eutonic solutions substantially coincide with the individual solubilities. The solubility of K_2SO_4 in an aqueous-saline solvent containing variable amounts of KSCN decreases, as would be expected, with rising concentration of KSCN. When the KSCN concentration in the liquid phase reaches slightly more than 46% by weight, almost complete

Composition of the System KCNS–K_2SO_4–H_2O (in weight %)

H_2O	KSCN	K_2SO_4	Solid phase	H_2O	KSCN	K_2SO_4	Solid phase
25° isotherm				40° isotherm			
89.24	–	10.76		86.90	–	13.10	
89.11	1.18	9.71		86.88	0.48	12.64	
88.55	3.03	8.42		86.03	2.10	11.87	
87.93	4.94	7.13		86.61	3.89	^ 50	
87.17	6.63	6.20		85.53	6.42	8.05	
86.08	8.68	5.24		85.47	8.12	6.41	
83.98	11.80	4.22		83.79	10.54	5.67	
81.91	15.04	3.05	K_2SO_4	82.89	11.94	5.17	
79.66	18.20	2.14		81.45	14.42	4.13	
74.48	24.07	1.45		77.64	19.31	3.05	K_2SO_4
66.90	32.50	0.60		73.85	24.46	1.69	
61.12	38.57	0.31		72.97	25.75	1.28	
53.65	46.15	0.20		68.92	30.06	1.02	
47.39	52.51	0.10		66.32	32.83	0.85	
				62.46	36.75	0.79	
29.36	70.60	0.04	K_2SO_4 + KSCN	59.93	39.63	0.44	
29.30	70.70	–	KSCN	53.48	46.30	0.22	
				43.97	55.9	0.13	
				25.73	74.24	0.03	K_2SO_4 + KSCN
				25.69	74.31	–	KSCN

...ting-out of the K_2SO_4 occurs, although up to the eutonic points considerable portions of the univariant curves still remain in both isotherms. Consequently, the solutions of KSCN only possess adequate solubility for K_2SO_4 over a specific range of concentrations. Since unsaturated solutions of KSCN with salt concentrations above 46% by weight, as well as the eutectic solutions, contain (as evident from the table) extremely small amounts of K_2SO_4 which lack practical significance.

The solubility of salts in water is dependent to a certain, not yet precisely established, degree on the interaction of ions of the dissolving salt with water molecules; the energetic characteristics for a given ion are determined by the value of its energy of hydration [2, 3]. In making a comparative evaluation of the experimental data for the solubility in the system $KSCN-K_2SO_4-H_2O$ we start from the premise that the solubilities of KSCN and K_2SO_4 in binary and ternary systems are fundamentally and specifically governed by the interaction of the anions with molecular water, the intensity of this interaction being determined not only by the charge but also by the structure of the ion [3]. In such an evaluation we may assume to a first approximation that the behavior of the common cation and its influence on the establishment of the equilibrium state in aqueous-saline systems in the given conditions do not depend on the anion forming a salt with the cation.



In the system which we have studied, the salts contain anions of differing structures. The triatomic anion SCN^- (with a linear configuration) contains —as follows from its electronic structure: $N:::C:\ddot{S}:$, —C as the central atom with a coordination number of 2 [4]. The C atom is compressed from two sides by the two non-identical hemispheres of the atoms of N and S which function in the KSCN structure as packing spheres. The distance between the atoms of N and S in the SCN^- group, judging by the radii of the covalent bond, is 2.96 A, which only differs slightly from the calculated distance of 2.94 A, obtained by X-ray investigation of potassium thiocyanate crystals [4]. Coupling of N, S and C atoms gives an anion of low symmetry, fairly long length and an evidently reduced effective action of the charge. Such an anion, considering also the special features of its structure, which are generalized in the linear configuration, is incapable of any considerable development of electrostatic forces, as adequately reflected in the low value of the hydration energy of SCN^-, equal to 72 kcal/g-ion and the m.p. of KSCN of 176° (low for ionic crystals).

The tetrahedral configuration of the SO_4^{2-} anion, unlike the SCN^- anion, has a well-defined general symmetry and, evidently, a symmetrical arrangement of the ionic charge in the space of the anionic group which consists of elements of similar properties. The magnitude of the hydration energy of the anion, equal to 243 kcal/g-ion, points to quite intensive interaction of SO_4^{2-} with molecules of water, although it does not lead to formation of thermodynamically stable complexes.

The high solubility of KSCN in water, in addition to other factors, bears a definite and specific relation to the weakness of the interaction of the SCN^- ion with molecules of water in solution, the degree of which interaction is greatly influenced by the above-outlined linear configuration of the anion. The bond energy of the SCN^- anion with water molecules may to some extent be compared to the energy with which water molecules are linked

to one another in the liquid state, i.e., the bonds developed between the anion and water molecules are unstable; they are often broken and formed again and lack a precise coördinative character. The SO_4^{--} anion, bearing in mind its double bond and high degree of symmetry, possesses a marked orientating action on water molecules, due to which the true value of the dielectric constant of water may be appreciably lowered. Consequently, among the factors determining the relatively low (for readily soluble salts) values of the solubility of K_2SO_4 at various temperatures, the most important is the intensive reaction of SO_4^{--} with molecules of water in solution.

It may be assumed that when ions of SO_4^{--} and SCN^- come into contact in ternary systems, the marked difference between their interactions with water molecules is maintained in full measure and that the actual influence of the common K^+ cation on the character of the interaction of each of the SO_4^{--} and SCN^- anions with molecules of water remains unchanged on transition from binary solutions to ternary solutions. As a general conclusion, we must emphasize that the markedly differing influence of the salts in the system $KSCN-K_2SO_4-H_2O$ on their joint solubility is a definite function of the difference in the behavior of the two anions toward molecules of water, and this behavior in turn is determined by the differing configurations of the anions.

SUMMARY

1. The solubility in the system $KSCN-K_2SO_4-H_2O$ was studied at 25 and 40°.

2. The necessity is noted of consideration of the structural data for the anions for characterization of the solubility in the binary and ternary aqueous-saline systems.

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INVESTIGATION OF METASTABLE EQUILIBRIA BETWEEN LIQUID PHASES. III.

I. L. Krupatkin

In the previous communications an examination was made of the theoretical bases for study of metastable equilibria between liquid phases; two types of these were studied and two new forms of equilibrium diagrams were obtained in this connection. The study of metastable liquid-phase equilibria in three-component systems revealed their close connection with solvent systems [1]. A more detailed elucidationof this connection necessitates a study of a ternary system in which one of the components is in the solid state and dissolves in the other two which are present in the given conditions in the liquid state. It is necessary to actualize the case of solubility of a solid in a liquid mixture of two solvents which do not form stable chemical compounds between themselves. A further requirement is that each of the solvents should form with the dissolved substance a system with metastable stratification. In these conditions we should come close to clarification of the very character of systems with metastable equilibrium between the liquid phases, to clarification of the behavior of compositions of such systems as a function of the temperature. The stated conditions are fulfilled, as preliminary experiments revealed, in the three-component system sulfur-diphenylamine-β-naphthylamine. The study of this sytem is the subject of this paper.

The only binary system involving these components that is mentioned in the literature is sulfur-diphenylamine [2]. Crystallization in this system takes place according to the usual eutectic type. The eutectic point is at 92% diphenylamine and 8% sulfur, and it corresponds to a temperature of 51.5°. Below the sulfur crystallization curve is the curve of the equilibrium between the liquid phases with an upper critical temperature of solution of 104°, corresponding to a composition of 32% diphenylamine and 68% sulfur. Above the stratification curve is a small horizontal portion of the crystallization curve of sulfur. The remaining two systems in the given ternary system —sulfur-β-naphthylamine and diphenylamine-β-naphthylamine —are investigated in this research. The system sulfur-β-naphthylamine is similar to the binary system sulfur-diphenylamine; in it is likewise established a metastable equilibrium between the liquid phases In the two-component system diphenylamine-β-naphthylamine no compound formation between the components is reflected on the curve of crystallization. In the liquid phase of this sytem, however, the existence of unstable compounds is possible since diphenylamine tended to form similar compounds, e.g., with quinoline.

Hence, in the three-component system sulfur-diphenylamine-β-naphthylamine we have solubility of the sulfur in a mixture of the two liquid amines (diphenylamine and β-naphthylamine) and dissociation of the associated sulfur in them. Both of the amines in the systems with sulfur form a metastable equilibrium between the liquid phases. Unstable complexes are possibly formed between the two amines. Thus, the given ternary system fully satisfies the above-indicated conditions.

EXPERIMENTAL AND EVALUATION OF RESULTS

The following reactants were taken for the investigation: sulfur recrystallized from benzene with m.p. 117°, and apparently consisting of a mixture of the monoclinic and rhombic forms [3]: diphenylamine, chemically pure, with m.p. 54°; β-naphthylamine "pure" with m.p. 112°.

The sulfur and diphenylamine were checked against the system sulfur-diphenylamine as detailed in the literature. The check showed agreement with the literature data. The research was carried out by Alekseev's method [4] in sealed ampoules in an oil thermostat.

System sulfur-β-naphthylamine was studied by fusion and stratifiability. The results are set forth in Table 1 and plotted in Figure 1. The fusion curve of this system has the usual eutectic form; the eutectic point is not low, has a composition of 35% β-naphthylamine and corresponds to a temperature of 100°. The sulfur crystallization curve has, above the curve of metastable stratification, a horizontal portion at 103° extending over the concentration range of 60 and 80% sulfur. Below the sulfur crystallization curve is the curve of metastable stratification with an upper critical solution temperature at 103.5°, displaced toward the sulfur corner, coinciding with the composition 75.05% sulfur and 24.95% β-naphthylamine.

Binary system diphenylamine-β-naphthylamine was studied by the fusion method. The results are set forth

TABLE 1

Equilibrium in the System Sulfur-β-Naphthylamine

No. of expt.	Sulfur (wt. %)	β-Naphthylamine (wt. %)	Temperature of crystallization	Temperature of stratification
1	0.00	100.00	112.0	–
2	13.05	87.00	107.0	–
3	20.56	79.44	104.5	–
4	30.00	70.00	102.0	
5	35.00E•	65.00	100.0	–
6	40.35	59.65	101.0	–
7	48.50	51.50	–	96.5
8	49.86	50.14	101.5	–
9	60.00	40.00	102.5	99.0
10	65.00	35.00	–	99.5
11	70.50	29.50	103.0	100.0
12	75.05	24.95	–	100.5
13	80.30	19.70	103.0	100.0
14	100.00	0.00	117.0	–

• = eutectic point

in Table 2 and plotted in Figure 2. The fusion curve of this system intersects the eutectic point at 42°, the composition then being 83% diphenylamine and 17% β-naphthylamine. Formation of chemical compounds between the components was not observed. Nevertheless, as indicated previously, unstable compounds are possible in this system in the liquid phase.

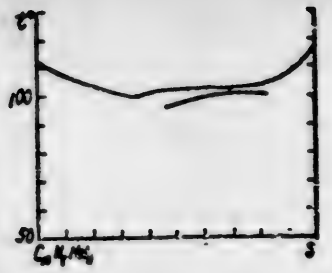

Fig. 1

Fig. 2

TABLE 2 Equilibrium in the System Diphenyl-[illegible]-Naphthyl[illegible]

No. of expt.	Diphenylamine (wt. %)	β-Naphthylamine (wt. %)	Crystallization temperature
1	0.00	100.00	112.0
2	9.64	90.36	105.0
3	19.14	80.86	100.0
4	29.95	70.05	94.5
5	40.00	60.00	88.0
6	49.92	50.08	81.0
7	59.90	40.10	71.0
8	69.99	30.01	60.5
9	75.00	25.00	54.5
10	80.00	20.00	46.5
11	83.00E•	17.00	42.0
12	85.06	14.94	44.0
13	90.11	9.89	47.0
14	95.00	5.00	50.0
15	100.00	0.00	54.0

• Eutectic point

The ternary system sulfur-diphenylamine-β-naphthylamine was studied by drawing polythermic sections through its prism, extending from the sulfur edge to the boundary of the binary system diphenylamine-β-naphthylamine. Six such sections were studied in all, with contents of 10, 20, 40, 60, 70 and 80% β-naphthylamine. Crystallization and stratification were studied in the polythermic sections. The data for the sections are set forth in Table 3 and plotted in Figure 3, a, b, c, d, e and f. In all the polythermic sections sulfur crystallizes with a very strong undercooling tendency, which is characteristic of systems with metastable equilibrium between the liquid phases, especially above the stratification curve. Due to this, some mixtures cannot be made to crystallize. These mixtures are indicated in the table. Each section consists of the crystallization curve of sulfur in the respective mixture of amines and the curve of metastable equilibrium between the liquid phases with the upper critical solution temperature, displaced to the sulfur corner. The metastability of the stratification in all the sections is an indication of the metastability of the whole equilibrium volume between the phases of the ternary system sulfur-diphenylamine-β-naphthylamine, i.e., of its existence entirely below the surface of crystallization of sulfur.

If the curve of the critical points is drawn through the critical points of the stratification curves of the binary systems and the sections, and if the same is done for the points of the fusion curve located above the critical points, then the projection of both curves on to the plane extending through the critical points of the binary systems will have the shape represented in Fig. 4. On this, the upper curve relates to crystallization and the lower one to metastable

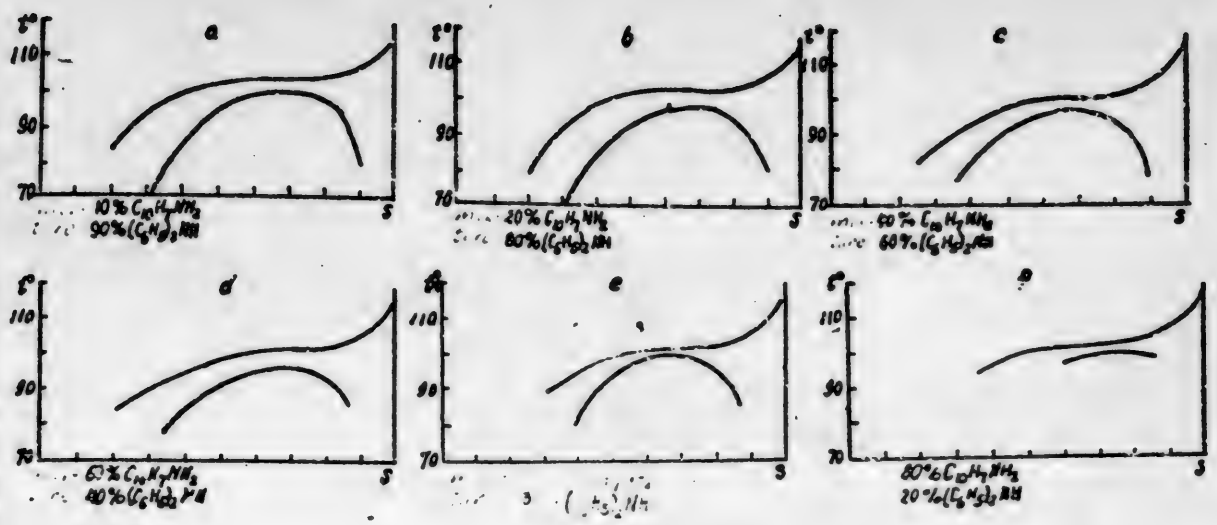

Fig. 3.

TABLE 3

Polytherms of the System Sulfur-Diphenylamine-β-Naphthylamine

No. of expt.	Sulfur (wt. %)	Temperature of crystallization	Temperature of stratification
Section No. 1: 10% β-naphthylamine, 90% diphenylamine			
1	19.88	84.0	—
2	29.82	94.0	70.0
3	39.99	99.5	86.0
4	50.00	103.0	94.5
5	60.11	103.5	99.0
6	70.00	104.0	100.0
7	80.06	105.0	99.0
8	84.91	—	94.0
9	89.89	107.0	80.0
Section No. 2: 20% β-naphthylamine, 80% diphenylamine			
1	20.00	79.0	—
2	29.84	92.0	—
3	31.07	—	81.0
4	39.97	99.0	85.0
5	50.00	101.5	93.0
6	60.60	103.0	—
7	61.99	—	97.0
8	69.39	103.0	99.0
9	80.00	104.0	96.5
10	85.65	105.0	92.0
11	86.99	—	89.0
12	87.99	106.0	87.0
13	90.00	—	81.0

No. of expt.	Sulfur (wt. %)	Temperature of crystallization	Temperature of stratification
Section No. 4: 60% β-naphthylamine, 40% diphenylamine			
1	19.92	84.0	—
2	30.00	89.0	—
3	34.90	—	79.0
4	40.11	94.0	85.0
5	50.00	98.0	91.0
6	60.07	101.0	95.5
7	69.95	does not crystallize	96.5
8	80.00	102.0	95.0
9	86.68	103.0	88.0
Section No. 5: 70% β-naphthylamine, 30% diphenylamine			
1	30.10	89.0	—
2	40.00	95.0	83.0
3	50.00	99.0	95.0
4	60.05	does not crystallize	99.0
5	69.90	102.0	99.0
6	79.97	103.0	97.0
7	85.03	—	92.0
8	87.00	104.0	88.0

TABLE 3 -- (continued)

No. of expt.	Sulfur (wt. %)	Temperature of crystallization	Temperature of stratification
	Section 3: 40% β-naphthylamine, 60% diphenylamine		
1	25.00	82.5	—
2	30.12	86.0	—
3	39.89	94.0	82.0
4	50.00	98.0	91.0
5	60.00	100.5	95.5
6	68.87	does not crystallize	96.0
7	80.19	101.0	94.0
8	85.65	—	91.0
9	90.00	105.0	79.0
	Section 6: 80% β-naphthylamine, 20% diphenylamine		
1	35.96	94.0	—
2	40.00	96.0	—
3	50.00	100.0	—
4	59.10	101.0	97.0
5	65.12	does not crystallize	98.0
6	75.00	ditto	99.0
7	80.13	103.0	99.0
8	85.65	—	98.0
9	90.00	106.0	—

stratification. This graph alone shows that the equilibrium space between the liquid phases of the ternary system has a saddle-like point. The saddle-like point has a temperature of 96° and occurs on the section of the ternary system containing 46% β-naphthylamine and 54 % diphenylamine in the two-component system — β-naphthylamine-diphenylamine. This composition corresponds to a 1:1 ratio between the molecules of the two amines (strictly it should be 45.83% β-naphthylamine and 54.17% diphenylamine). The projection of the crystallization curve likewise has a minimum which falls on the same section of the ternary system at a temperature of 101°. Both curves exhibit the general course of crystallization and stratification.

Starting from the polytherms of metastable equilibrium between the liquid phases, the stratification isotherms represented in Fig. 5 were plotted. A total of 4 isothermal sections was plotted through the prism of the ternary system at temperatures of 90°, 95°, 97° and 100°. The 97° and 100° isotherms are above the saddle-like point and therefore they possess two separate regions of stratification. The latter start from solubility breaks at the corresponding temperatures in the two-component systems with metastable equilibrium between the liquid phases present inside the prism and they later merge. At 96°, i.e., the temperature of the saddle-like point, they must come into contact with each other. The 90° and 95° isotherms are below the saddle-like point. Hence, in these isothermal sections both regions of stratification, starting from the solubility break in the binary systems, run together inside the prism of the ternary system into one region of stratification of the ternary system. The isotherms of metastable stratification located below the saddle-like point possess maxima of reciprocal solubility of sulfur and mixtures of the amines in the liquid state. These maxima coincide with the polythermal section which, in the binary system, diphenylamine-β-naphthylamine corresponds to the 1:1 molar ratio.

Starting from the crystallization polytherms, plots were constructed of the isotherms of crystallization of sulfur in the ternary system. A total of 5 such isothermal sections was drawn through the prism of the ternary system at temperatures of 85°, 90°, 95°, 100° and 105°. The isotherms are shown in Fig. 6. They all have a similar form with a maximum of solubility of sulfur in the mixture of amines. These maxima fall on the very same polythermal section as the maxima of mutual solubility of the components in the liquid state, namely on the section corresponding in the binary system of the two amines to 1:1 molar ratios

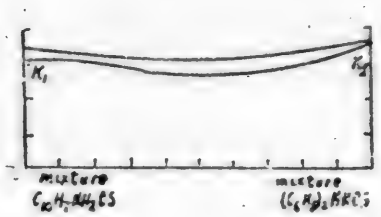

Fig. 4.

The foregoing graphical data permit the representation of the three-component system sulfur-diphenylamine-β-naphthylamine in the form of a prism. This is illustrated in Fig. 7, where B, C, and D respectively denote β-naphthylamine, sulfur and diphenylamine. The diagram clearly shows the space of the two-phase liquid state 1, 2, 3, 4, K_1, K_2, metastable at all temperatures and concentrations, with a saddle. The surface of crystallization of sulfur 5, 6, 7 is observed with its solubility maximum in mixtures of the two amines — diphenylamine and β-naphthylamine.

Consequently, the two-component system β-naphthylamine-diphenylamine is a typical solvent system in relation to sulfur, both

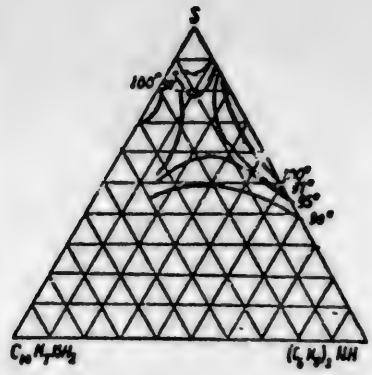

Fig. 5

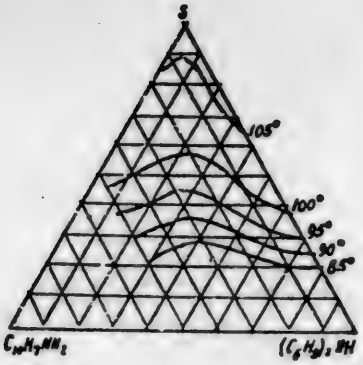

Fig. 6

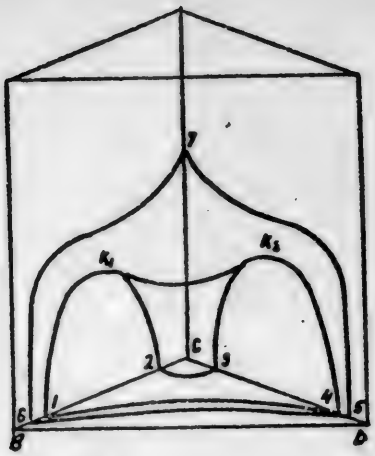

Fig. 7

in its liquid and solid state. Indeed at 95°, for example, the solubility of liquid sulfur in the separate amines is of the order of 45%, whereas in the 1:1 molar mixture of the amines—in which the solubility of sulfur reaches a maximum—the solubility approaches 60%. At the same temperature the solubility of solid sulfur in the amines is only of the order of 30%, but in the 1:1 mixture it reaches 45%. On the basis of the theory of solubility developed by R. V. Mertslin [1], these facts may find an explanation in the following way. First, in the binary system β-naphthylamine-diphenylamine, a chemical compound is formed with 1:1 molar composition. Second, this compound is unstable and easily breaks down at higher temperatures even in such a nonpolar solvent as sulfur. This evidently accounts for the absence of a maximum on the fusion curve of the two-component system diphenylamine-β-naphthylamine. Third, sulfur in the associated state is not passive toward the specified compound and dissociates therein. In this latter connection, we may recall that the dissociation of associated sulfur in amines is a well-known phenomenon.

All the above-stated facts become fully understandable on the assumption of formation of a solvent system. However, an additional factor is necessary for development of solvent systems. This is a type of monotectic crystallization in the three-component system such that crystallization of one and the same component should take place throughout the whole region from one stratifying binary system (in the ternary system in question) to the other. Monotectic crystallization takes place when there is stable stratification in a system, when the curves or surfaces of stratification intersect the curves or surfaces of crystallization and one of the phases of the system disappears with change of temperature. In the case of the three-component system sulfur-diphenylamine-β-naphthylamine, throughout the whole region between the two binary systems with metastable stratification we find crystallization of one and the same component, namely sulfur; here, however, the crystallization is not monotectic since the whole surface of stratification is metastable and does not intersect the surface of crystallization. Nevertheless, as shown by the isotherms of crystallization, the solvent character of the system is also realized at temperatures above the critical temperatures of the metastable equilibrium between the liquid phases. This fact suggests that in a series of cases the two-component systems with metastable stratification may behave like systems with stable equilibrium between the liquid phases. We may, therefore, conclude that in the given systems with metastable stratification at temperatures very much higher than the temperatures of stratification, we obtain a state close to the state of latent stratification. It is clear that compositions in the latently stratified state may often behave like compositions with normal stratification.

The above discussion permits us to explain the process of development of metastable stratification. It must proceed from true homogeneity to latent stratification and from the latter to metastable stratification. The possibility of development of stable stratification by this route is not excluded.

On the basis of the above experimental material we may approach certain problems of prognosis of solvent systems. Clarification of the conditions of formation of solvent systems is particularly important due to its potential practical value in the selection of solvent systems for certain substances for which single solvents cannot be readily found. These problems were analyzed by R. V. Mertslin [1] for ternary systems involving

binary systems with stable equilibrium between the liquid phases, [illegible] tion arises in two binary systems entering into the given ternary system and where there is compliance with the other factors necessary for formation of a solvent system, then such a system is actually developed. From this it follows that if a given binary system contains associated components capable of dissociating in each other or of forming a chemical compound susceptible to mutual dissociation with the dissolved substance, and if its components form binary systems with it with metastable stratification, then we can expect the development of a solvent system.

SUMMARY

1. The binary system sulfur-β-naphthylamine was investigated by the fusibility and stratification methods. The fusion data point to a eutectic form of fusion diagrams. Below the crystallization curve of sulfur is seen a stratification curve; the stratification is metastable at all temperatures and concentrations.

2. The system diphenylamine-β-naphthylamine was investigated by the fusion method. Its equilibrium diagram is of the eutectic type.

3. The equilibrium of the solid and liquid phases in the ternary system sulfur—diphenylamine—β-naphthylamine was investigated. The system contained a field of the two-phase liquid state, metastable at all temperatures and concentrations, with a saddle point, starting from the plane of metastable stratification of its binary systems sulfur-diphenylamine and sulfur-β-naphthylamine.

4. Suggestions are made about the possible mode of development, from the homogeneous solution, of metastable stratification and about its behavior at higher temperatures.

5. Some supplementary conditions for the practical choice of solvent systems are indicated.

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INVESTIGATION OF THE INTERACTION BETWEEN QUINOLINE AND NITROPHENOLS BY THE METHODS OF PHYSICO-CHEMICAL ANALYSIS

A. D. Kirillova and D. E. Dionisyev

Quinoline resembles pyridine [1, 2] in being a good complex-former due to the presence of a tertiary nitrogen atom which serves as an electron donor. Investigation of the interaction of quinoline with phenol by the fusion and viscosity methods [3] revealed the existence of highly dissociated compounds with the composition: $C_9H_7N \cdot 2C_6H_5OH$ and $3C_9H_7N \cdot 2C_6H_5OH$.

We set ourselves the problem of establishing the nature of the influence on the character of the interaction of the introduction of nitro groups into various positions of the phenol molecule; also the effect of the number of such groups. With this objective we studied the interaction of quinoline with o- and p-nitrophenols and with 2,4-dinitrophenol by the methods of fusion, viscosity, density and electrical conductivity.

For the investigation we used chemically pure quinoline which, after prolonged standing over KOH and two fractional distillations, had b.p 238°, d_4^{45} 1.077, η^{45} 1.890.

o-Nitrophenol, recrystallized three times from alcohol, m.p. 44.5°, d_4^{45} 1.286, η^{45} 2.030.

p-Nitrophenol, recrystallized three times from water, had m.p. 113°, d_4^{115} 1.280, η^{115} 2.900.

2,4-Dinitrophenol twice recrystallized from alcohol, had m.p. 113.3°, d_4^{115} 1.440, η^{115} 2.990.

The system quinoline–o-nitrophenol was investigated by Bramley [3] by the colorimetric method and by the fusion method at temperatures of 30, 40, 60, and 80°. The maxima on the viscosity curves occur at approximately 58.2 wt-% o-nitrophenol. On the basis of investigation by these methods, Bramley [3] comes to the conclusion that a molecular compound with the composition $C_9H_7N \cdot o\text{-}C_6H_4NO_2OH$ is formed. We performed an investigation of the fusion and electrical conductivity and repeated the investigation of the density and viscosity. We failed to detect the formation of a chemical compound of definite composition by the fusion method, since in the 55 to 85 mole-% range of quinoline, non-crystallizable, vitreous masses were formed (Fig. 1). The density isotherms (Fig. 2) at 45 and 55° are very slightly concave to the axis of composition of the curves. The isotherms of viscosity η at the same temperatures are curves with small, diffused maxima. The curve of the absolute temperature coefficient of viscosity α has a maximum corresponding to the composition of 50 mole% quinoline. The electrical conductivity κ was plotted at 25, 45, and 55° (Fig. 3). The electrical conductivity of the mixture rises considerably in comparison with the pure components, reaching a maximum of about 40 mole% quinoline. Correction of the electrical conductivity for viscosity $\eta\kappa$ hardly changes the position of the maxima. We also incline to the view that in this system a strongly dissociated chemical compound of the composition $C_9H_7N \cdot o\text{-}C_6H_4NO_2OH$ is formed and that the maxima of the curves of electrical conductivity and corrected conductivity $\eta\kappa$ are shifted in the direction of o-nitrophenol from the ordinates of the compound. By comparison with the system quinoline–phenol the present system has a lower viscosity, but the electrical conductivity and the corrected conductivity are considerably higher.

The system quinoline–p-nitrophenol has not previously been investigated. The fusion curve (Fig. 4) has a maximum corresponding to 50 mole-% quinoline with m.p. 89.5°, which indicates formation of a solid phase compound of the composition $C_9H_7N \cdot p\text{-}C_6H_4NO_2OH$.

The density isotherms (Fig. 5) are concave to the axis of composition of the curves without any maxima. The viscosity isotherms are concave to the axis of composition in the p-nitrophenol region, pass through a maximum and are convex to the axis of composition in the quinoline region. The maxima flatten out with rising temperature. The curves of the absolute temperature coefficient of viscosity are similar to the viscosity isotherms. The viscosity curves suggest a chemical reaction in the system but the maxima are not correlated with the composition of a chemical compound. The isotherms of electrical conductivity (Fig. 6) rise steeply from p-nitrophenol, forming

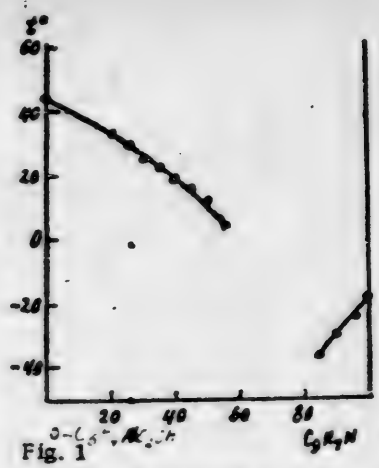

Fig. 1

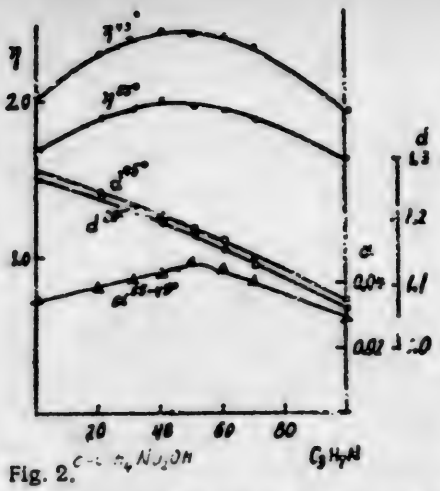

Fig. 2.

oline at which point they become convex to the axis of composition. Usanovich [4] regards such curves as evidence of acid-base interaction, but the position of the maximum makes it difficult to draw any conclusion about the composition of the chemical compound. Possibly, in the liquid phase another, strongly dissociated, compound is formed which is incapable of crystallization; composition: $C_9H_7N \cdot 2p\text{-}C_6H_4NO_2OH$.

This compound is reflected on the isotherms of viscosity, electrical conductivity and corrected electrical conductivity in the form of maxima shifted in the direction of p-nitrophenol. We see that in this system the viscosity, electrical conductivity and corrected electrical conductivity are considerably higher than in the preceding systems.

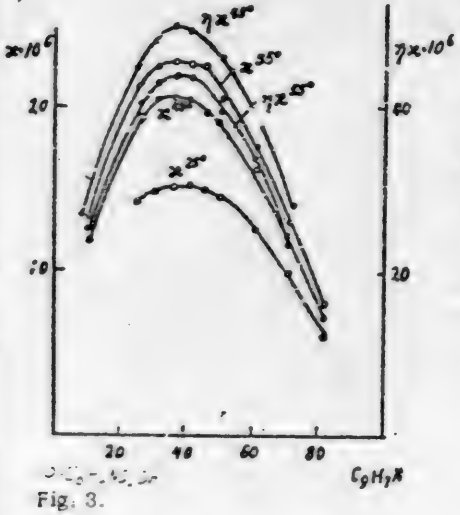

Fig. 3.

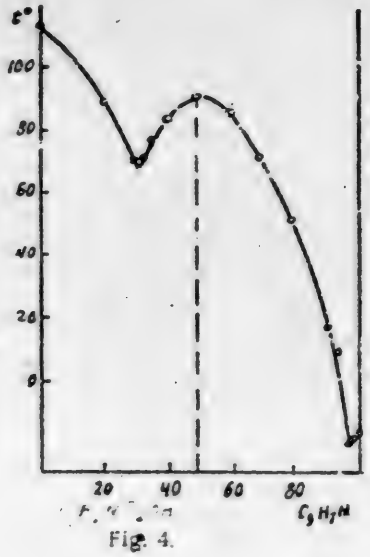

Fig. 4.

The system quinoline–2,4-dinitrophenol was also investigated by us for the first time. The melting point curve (Fig. 7) forms a maximum corresponding to 50 mole-% quinoline, which testifies to the formation of the compound $C_9H_7N \cdot 2\text{-}C_6H_3(NO_2)_2OH$.

The density isotherms (Fig. 8) are curves which are concave to the axis of composition, indicating dissociation in the system. The viscosity isotherms have the same form as in the preceding system. The viscosity maximum at 95° corresponds to approximately 40 mole-% 2,4-dinitrophenol and with rising temperature it is shifted in the direction of the more viscous component (dinitrophenol). The curves of the absolute temperature coefficient of viscosity repeat the course of the viscosity curves and the maxima are formed at the same compositions. The maxima of the electrical conductivity isotherms (Fig. 9) are at 125° and 50 mole-% quinoline. With rising temperature the maxima are shifted in the quinoline direction. This displacement is accounted for by the increasing viscosity of the mixtures with falling temperature, due to which the maxima of electrical conductivity are shifted in the direction of compositions with a lower viscosity. The correction of the electrical conductivity for viscosity did not change the course of the curves which were only slightly shifted in the direction of 2,4-dinitrophenol. The curves of viscosity and electrical conductivity reflect the existence of the compound which was detected by the fusion method. The values of viscosity, electrical conductivity and corrected electrical conductivity exceed those of the preceding systems.

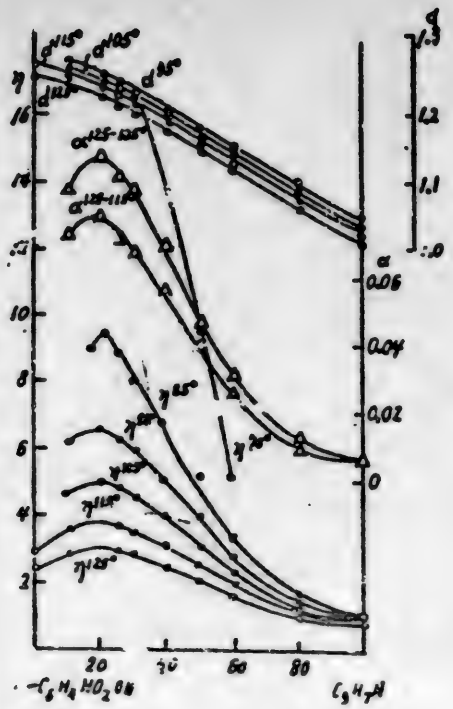

Fig. 5.

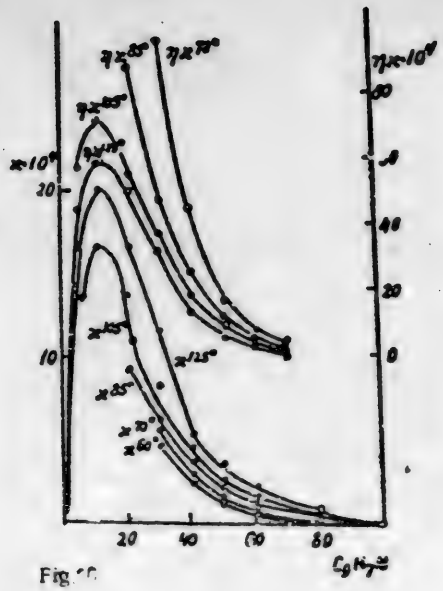

Fig. 6.

SUMMARY

1. The isotherms of viscosity, density, electrical conductivity and corrected electrical conductivity of the systhem quinoline–o-nitrophenol point to formation of an equimolecular compound in the liquid phase.

2. The fusion method demonstrated the formation in the system quinoline–p-nitrophenol of an equimolecular compound. The isotherms of viscosity, density, electrical conductivity and corrected electrical conductivity point to the occurrence of chemical interaction in the system, but the maxima of the curves are not correlated with the composition of a compound.

Fig. 7.

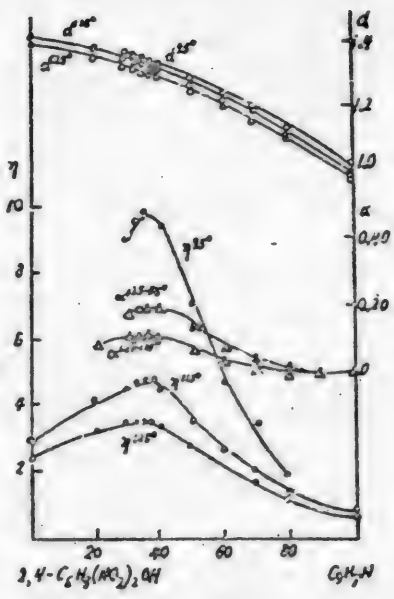

Fig. 8.

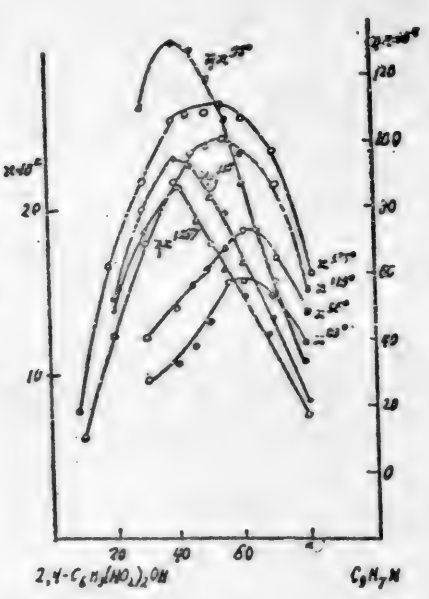

Fig. 9.

3. In the system quinoline–2,4-dinitrophenol the fusion method established the existence of an equimolecular compound. On the isotherms of viscosity, electrical conductivity and corrected electrical conductivity is reflected the existence of the compound detected by the fusion method.

4. The p-position of the nitro group in phenol intensifies the interaction with quinoline in comparison with the o-position due to the formation in o-nitrophenol of an internal hydrogen bond which hinders interaction (the ortho effect). Introduction into the phenol molecule of a second nitro group still further intensifies the interaction.

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* See Consultants Bureau Translation, p. 2143.

INVESTIGATION OF THE INTERACTION OF QUINOLINE WITH α- AND β-NAPHTHOLS BY THE METHODS OF PHYSICO-CHEMICAL ANALYSIS

A. D. Kirillova and D. E. Dionisyev

Using the methods of fusion, viscosity, density and electrical conductivity, we have studied the systems quinoline-α-naphthol and quinoline-β-naphthol which have not previously been investigated.

System quinoline-α-naphthol. The fusion curve (Fig. 1) forms one maximum corresponding to 50 mole-% quinoline and one transition point corresponding to 72 mole-% quinoline with a transition temperature of 29°, which indicates formation of two compounds: one melting congruently, corresponding to the composition $C_9H_7N \cdot \alpha\text{-}C_{10}H_7OH$ and having an m.p. of 53.5°; the second melting incongruently and with a composition difficult to determine accurately; possibly it is the compound $2C_9H_7N \cdot \alpha\text{-}C_{10}H_7OH$ or $3C_9H_7N \cdot 2\alpha\text{-}C_{10}H_7OH$.

The curves of the density isotherms (Fig. 2) are concave to the axis of composition. The curves of the viscosity isotherms have maxima which flatten out with rising temperature. We attempted to plot the viscosity isotherm at a temperature below the melting point of the compound. At 50° the viscosity maximum corresponds to approximately 45 mole-% quinoline; with rising temperature it is appreciably shifted in the direction of α-naphthol. Such a large shift of the viscosity maximum from the ordinates of the compound, even at a temperature below the melting point of the compound, indicates that the compound breaks down when still in the solid phase. The curves of the absolute temperature coefficient of viscosity α have the same forms as the viscosity isotherms.

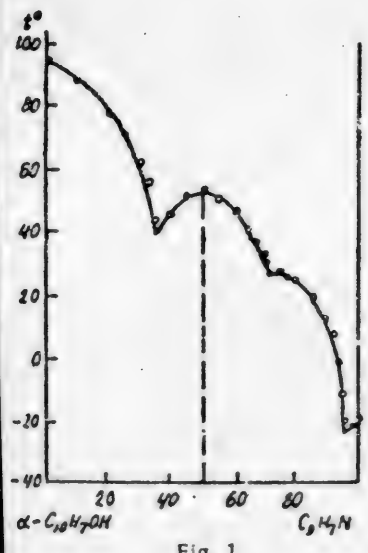

Fig. 1

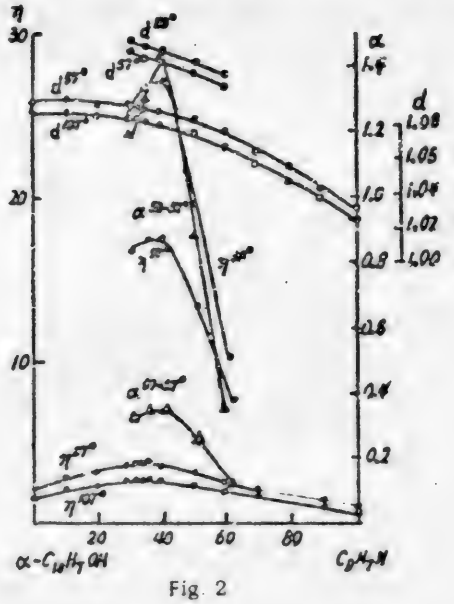

Fig. 2

The isotherm of electrical conductivity κ (Fig. 3) at 107° has a maximum corresponding to 35 mole-% quinoline. With falling temperature an inflexion starts to form (at 97°), leading to a minimum (at 77°) which becomes more pronounced with falling temperature (57°). As we know, systems in which conductive mixtures are developed from two nonconductive substances belong to the 7th type in M. A. Klochko's classification [1]. When the correction for viscosity (ηκ) is made, the maximum of electrical conductivity may pass into a minimum with falling temperatures (due to the greatly increased viscosity). The given system vividly illustrates the

[illegible] maximum of electrical conductivity into a minimum due to the rise in viscosity. The position of the minimum of electrical conductivity indicates the formation in the system of the compound $C_9H_7N \cdot \alpha\text{-}C_{10}H_7OH$. The correction of the electrical conductivity for viscosity shifts the maximum of electrical conductivity in the direction of quinoline. Thus, at 57° the maximum corresponds to 40 mole-% quinoline, but with rising temperature it moves in the direction of α-naphthol. From a study of the liquid phase we may conclude that the diagrams of state reflect a more stable equimolecular compound. No sign of a second compound is found.

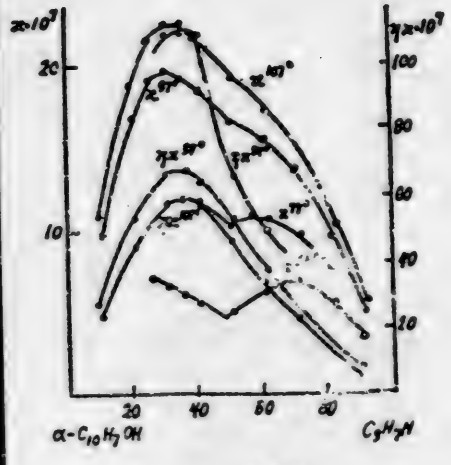

Fig. 3.

Fig. 4.

System quinoline-β-naphthol. The fusion curve (Fig. 4) has two transition points, corresponding to 34 mole-% quinoline with m.p. 71.5° and to 51 mole-% quinoline with m.p. 55°. The transition points nearly coincide with the ordinates of the compounds $C_9H_7 \cdot 2\beta\text{-}C_{10}H_7OH$ and $C_9H_7N \cdot \beta\text{-}C_{10}H_7OH$. Cases of coincidence of transition points with the ordinates of composition of compounds are met with fairly often in the literature [2,3].

The curves of the density isotherms (Fig.5) are also concave to the axis of compositions. The viscosity isotherms at 105, 115 and 125° have maxima in the region of 30 mole-% quinoline and they flatten out with rising temperature. On the 70 and 90° isotherms, which we plotted in the undercooled state of the system, the composition of the maximum could not be determined because mixtures up to 35 mole-% quinoline (at 75°) and 40 mole-% quinoline [illegible] crystallized. It is clear, however, from the course of the curves that the maximum lies between 30 and 35 mole-% quinoline. The curves of absolute temperature coefficient of viscosity repeat the course of the isotherms of viscosity and form maxima at the same compositions. We are therefore justified in [illegible] that the viscosity diagrams reflect one of the compounds detected by the fusion method, [illegible] $C_9H_7N \cdot 2\beta\text{-}C_{10}H_7OH$. The electrical conductivity isotherms, measured at the same temperatures as for viscosity, [illegible] consist of curves with maxima corresponding to approximately 25 mole-% quinoline. The electrical measurements [illegible] temperatures below the melting points of the compound (50, 70°) indicate that the [illegible] compound is not reflected on the electrical conductivity diagram. The viscosity correction did not change the course of the curves.

SUMMARY

1. Two compounds are detected in the system quinoline – α-naphthol by the fusion method: the first melting congruently, $C_9H_7N \cdot \alpha\text{-}C_{10}H_7OH$ and $2C_9H_7N \cdot \alpha\text{-}C_{10}H_7OH$ or $3C_9H_7N \cdot 2\alpha\text{-}C_{10}H_7OH$. The isotherms of viscosity, electrical conductivity and corrected electrical conductivity of the system quinoline – α-naphthol point to the existence in the liquid phase of a compound of the composition $C_9H_7N \cdot \alpha\text{-}C_{10}H_7OH$. No reflection of the second compound appears on the isotherms in question.

2. In the system quinoline – β-naphthol, by the fusion method, was detected the formation of two incongruently melting compounds, $C_9H_7N \cdot \beta\text{-}C_{10}H_7OH$ and $C_9H_7N \cdot 2\beta\text{-}C_{10}H_7OH$. Only one compound, with the composition $C_9H_7N \cdot 2\beta\text{-}C_{10}H_7OH$, is reflected on the diagrams of viscosity, electrical conductivity and corrected electrical conductivity.

3. The density isotherms of both systems consist of curves which are concave to the axis of compositions, indicating that contraction had occurred in the system.

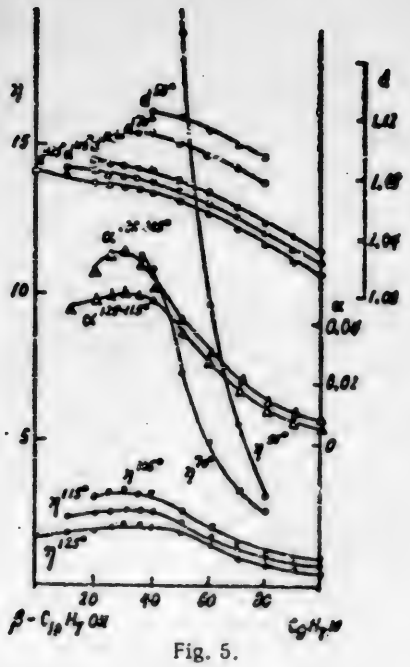

Fig. 5.

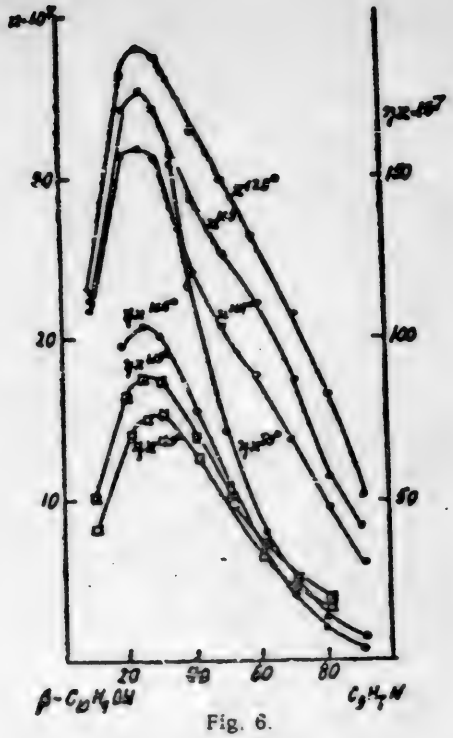

Fig. 6.

4. Introduction into the phenol molecule of an additional benzene ring weakens the interaction with quinoline. Evidently the weakening of the complex-forming properties is caused, apart from the high dissociation constant of naphthol, by steric hindrance. The β-position in naphthol is more favorable to complex formation than the α-position (the viscosity, electrical conductivity and corrected electrical conductivity are higher in the case of β-naphthol).

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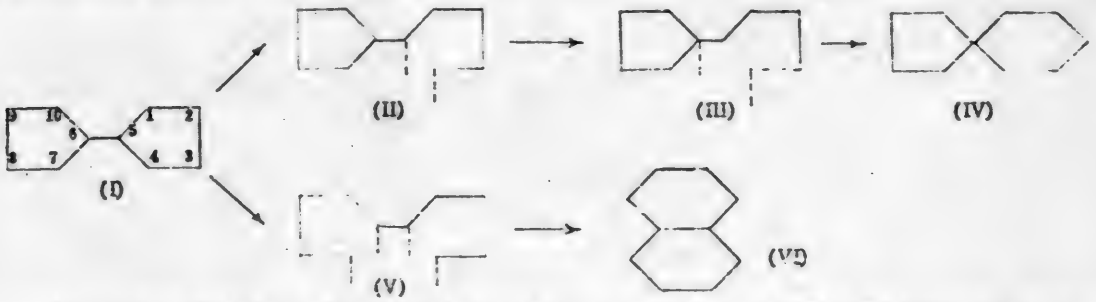
ISOMERIZATION OF POLYMETHYLENE HYDROCARBONS UNDER THE INFLUENCE OF ALUMINUM CHLORIDE

XVIII. ISOMERIZATION OF DICYCLOPENTYL

M. B. Turova-Polyak, I. E. Sosnina and E. G. Treshchova

The isomerization of hydrocarbons of the cyclopentane series by their interaction with aluminum chloride has been very completely studied and elucidated in the literature. The action of aluminum chloride on bicyclic hydrocarbons of this series, in particular on dicyclopentyl, has only been studied in cracking conditions [1]. N.D. Zelinsky and I. N. Tits [2] observed enlargement of the ring system of dicyclopentyl into the decahydronaphthalene system by the action of hydrogen iodide on cyclopentylcyclopentanol. A similar phenomenon was observed in the present research on dehydration of cyclopentylcyclopentanol with concentrated phosphoric acid. Decahydronaphthalene was detected among the products of hydrogenation of cyclopentylcyclopentene. The aim of this investigation was the study of the isomerizing action of aluminum chloride on dicyclopentyl.

Regarding dicyclopentyl as a monosubstituted cyclopentane, it was natural to assume that the products of its isomerization would be either spiro-(4,5)-decane, due to enlargement of one of the five-membered rings, or decahydronaphthalene, due to simultaneous enlargement of both five-membered rings. Formation of spiro-(4,5)-decane and decahydronaphthalene from dicyclopentyl could be represented by the following scheme:



According to this scheme, formation of spiro-(4,5)-decane may be explained in the following manner: The bond between carbon atoms 4 and 5 (II) is first ruptured. Then the hydrogen atom of carbon atom 6 migrates to carbon atoms 5 (III) and, finally, a new bond is formed between carbon atoms 6 and 4 (IV). According to the above scheme, decahydronaphthalene may be formed by simultaneous rupture of the bonds between carbon atoms 4,5 and 6,7 (V) and formation of fresh bonds between carbon atoms 4,6 and 5,7 (VI).

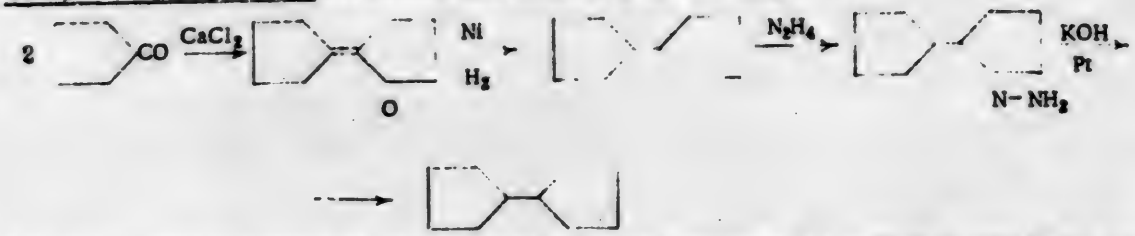
Our investigation revealed that the interaction of dicyclopentyl with aluminum chloride proceeds with considerable evolution of heat. In the couse of $1\frac{1}{2}$ minutes the temperature rises from room temperature to 100-103°, after which it gradually falls. The sole product of isomerization of dicyclopentyl is decahydronaphthalene, predominantly in the trans-form. The presence of decahydronaphthalene was demonstrated by formation of naphthalene on dehydrogenation of the isomerization products and was confirmed by the Raman spectrum. The predominance of trans-decahydronaphthalene among the products of isomerization is in good accord with earlier data of N.D. Zelinsky and M. B. Turova-Polyak [3] who showed that interaction of cis-decahydronaphthalene with aluminum chloride at room temperature gives mainly trans-decahydronaphthalene. It is interesting to note that the hydrocarbon fractions obtained on isomerization of cis-decahydronaphthalene had constants [3] similar to those of the hydrocarbon fractions obtained on isomerization of dicyclopentyl.

Spiro-(4,5)-decane, whose formation should result from enlargement of one five-membered ring, was not detected among the reaction products. It has thus been established that the bicyclic system of dicyclopentyl, under the influence of aluminum chloride, just as readily undergoes isomerization with enlargement of the five-membered rings as do monocyclic hydrocarbons of the cyclopentane series.

This very type of isomerization possibly occurs in the conditions of petroleum deposits, and would then account for the absence from petroleums of such hydrocarbons as dicyclopentyl and for the presence of decahydronaphthalene.

EXPERIMENTAL

The synthesis of dicyclopentyl was accomplished according to the following scheme:



2-Cyclopentylidene-cyclopentanone was prepared by boiling cyclopentanone in a Soxhlet apparatus in presence of calcium carbide for 4 hours [1]. The ketone distilled at 128-130° (21 mm) and had n_D^{20} 1.5196; d_4^{20} 1.0221 (yield 54%).

2-Cyclopentyl-cyclopentanone was prepared in 86% yield by hydrogenation of 2-cyclopentylidene-cyclopentanone at room temperature in presence of skeletal nickel and at 2 hydrogen pressure of 90-107 atm. Its constants were: b.p. 107-109° (13 mm); n_D^{20} 1.4772; d_4^{20} 0.9775. MR_D 43.84; calculated 43.99. The semicarbazone of cyclopentyl-cyclopentanone melted at 209° after two recrystallizations from ethyl alcohol.

The m.p. of this semicarbazone is also given by Venus-Danilova [4] as 209°.

Dicyclopentyl was prepared by decomposing the hydrazone of 2-cyclopentyl-cyclopentanone by Kizhner's method. Yield of hydrocarbon 92% calculated on the 2-cyclopentylcyclopentanone. The high yield of hydrocarbon was due to the introduction into the reaction of a fivefold excess of hydrazine hydrate and to prolonged heating of the reaction mixture (14 hours on water bath and 6 hours on an oil bath at bath temp. of 130-140°).

Traces of base were removed from the prepared dicyclopentyl by washing first with acetic acid and then with dilute sulfuric acid. The dried hydrocarbon distilled over metallic sodium at 188.5-189° (748 mm) and n_D^{20} 1.4650; d_4^{20} 0.8658. MR_D 44.06; calculated 43.98. Yield of dicyclopentyl 53% on the cyclopentanone taken in the reaction.

Dicyclopentyl was examined by the Raman spectrographic method. The intensity of the lines was determined visually and evaluated according to the conventional scale.

Spectrum of dicyclopentyl: 221 (0.5); 257 (1); 276 (1); 321 (9); 345 (1.5); 401 (2.5); 520 (1); 586 (1); 701 (0); 769 (0); 793 (1.2); 859 (1); 865 (2); 893 (10; r); 963 (2); 979 (1); 1022 (5; r); 1056 (1); 1103-1107 (2.5; vb); 1144 (1); 1170-1196 (2.5; d); 1275 (1.5; r); 1318 (2.5); 1364 (1.8); 1389 (1); 1445 (10); 1465 (1.5).

The spectrum of dicyclopentyl obtained in the present research agrees almost completely with the Raman spectrum obtained by Levina and co-workers [5] for dicyclopentyl prepared by the action of magnesium on cyclopentadiene hydrochloride followed by hydrogenation of the $\Delta^{2,2'}$-dicyclopentenyl.

In view of the fact that it was proposed to use in our investigation the method of catalytic dehydrogenation, it was necessary to clarify the behavior of dicyclopentyl in the conditions of this reaction. Dicyclopentyl was led over 2% platinized carbon at 300-305° without addition of hydrogen from outside. The catalyzate, obtained after the first pass, had refractive index n_D^{20} 1.4577 (original hydrocarbon had n_D^{20} 1.4650); after a second pass it had n_D^{20} 1.4518, and after a third pass n_D^{20} 1.4487. It was thus established that in the specified conditions dicyclopentyl undergoes hydrogenolysis. The same pattern of change of refractive index of dicyclopentyl was observed in the conditions of catalytic dehydrogenation by N. D. Zelinsky and I. N. Tits in the above-cited paper [2].

Isomerization of dicyclopentyl. The apparatus used was the same as in preceding researches [6]. A constant molar ratio of aluminum chloride to hydrocarbon was used in each experiment (1:3). The aluminum chloride was sublimed immediately before each experiment and did not change its external appearance during use.

Experiment 1. The reaction set in immediately after addition of the dicyclopentyl to the aluminum chloride. After 1½ minutes the temperature had risen to 100-103°, after which it began to fall gradually and 20-30 minutes later it had fallen to the original room temperature. No gaseous reaction products were evolved. After termination of the

reaction, the hydrocarbon layer (89%) was decanted from the aluminum chloride, washed, dried and distilled over sodium. A portion of the reaction product was then examined by the Raman spectrographic method; another portion was subjected to fractionation and then to dehydrogenation. The data for fractional distillation are set forth in Table 1.

The constants of the obtained hydrocarbon fractions proved to be so close to the constants of dicyclopentyl and the possible products of isomerization (decahydronaphthalene and spirodecane, Table 2) that it was difficult to assess the extent of the reaction from them.

The small amount of the first fraction only permitted us to carry out the elementary analysis; this indicated that it was a product of isomerization of dicyclopentyl.

5.655 mg substance: 18.017 mg CO_2; 6.610 mg H_2O. 6.148 mg substance: 19.560 mg CO_2; 7.275 mg H_2O. Found %: C 86.91, 86.32; H 13.08, 13.24. $C_{10}H_{18}$. Calculated %: C 86.87; H 13.13.

Dehydrogenation of the second and third fractions, carried out in conditions similar to those for the dehydrogenation of dicyclopentyl, gave naphthalene.

Spectrum of product of isomerization of dicyclopentyl: 247 (0.3; r); 299 (1.5); 349 (1.5), 397 (1); 409 (12); 434 (1); 493 (5); 558 (0.5); 578 (1); 629 (0.5); 644 (0.5); 695 (1); 718 (1; d); 753 (5); 792 (0.8); 822 (0.8); 846 (4); 875 (2); 896 (0.8); 930 (0.5); 956 (0.5); 994 (2.5; r); 1040 (1); 1056 (11); 1085 (1.5; d); 1093 (0.5); 1143 (1); 1165 (5); 1196 (0.5); 1227 (2); 1256 (8); 1267 (1); 1309 (0.5); 1347 (1.5); 1356 (2.5); 1384 (1); 1443 (10); 1460 (1.5).

In the spectrum of the product of isomerization of dicyclopentyl were detected all the lines characteristic, according to Fenske [10], of trans-decahydronaphthalene. They are the strongest lines of our spectrum. The presence of weaker lines, not observed by Fenske in the spectrum of trans-decahydronaphthalene, may be explained by the limitations of Fenske's procedure which did not permit the recording of weaker lines in the spectrum. According to Fenske the strongest lines in the spectrum of cis-decahydronaphthalene are 594 (3.39); 741 (6.12); 1037 (4.66) and 1.. (4). The spectrum that we obtained contained only a weak line 1040 (1); the remaining intense lines of cis-decahydronaphthalene were not detected. This indicates the absence from our reaction product of any considerable amount of cis-decahydronaphthalene.

The most intense lines of spiro-(4,5)-decane, according to M. T. Batuev [11], are 1024 (131) and 1037 (131); medium-intensity lines are at 302 (89), 519 (81), 714 (81) and 993 (85). The lines at 299, 718, 994 and 1040 obtained in our spectrum cannot be regarded as the lines of spiro-(4,5)-decane at 302, 714 and 993 cm^{-1}, since the intense lines of spiro-(4,5)-decane at 519 and 1024 are absent.

To dicyclopentyl may belong the 896 (0.8) line whose feeble intensity suggests that dicyclopentyl is only present among the reaction products in insignificant amounts.

Consequently, from a comparison of the spectrum of the product of isomerization of dicyclopentyl with the spectra of dicyclopentyl, cis- and trans-decahydronaphthalene and spiro-(4,5)-decane it follows that the products of our reaction consist in the main of the trans form of decahydronaphthalene; spiro-(4,5)-decane is absent and dicyclopentyl is present in insignificant amount.

Experiment II. In the second experiment the reaction mixture, after the rise of temperature, was heated for 15 hours on a water bath. This enabled clarification of the influence of prolonged heating on the interaction of aluminum chloride with dicyclopentyl. The reaction products (84%) were worked up and fractionated as in the first experiment. The fractionation data are set forth in Table 1. The prolonged heating resulted in the appearance among the reaction products of a lower boiling fraction (180-182°, 9%), testifying to the more drastic modification of the molecule of dicyclopentyl. Dehydrogenation of this fraction yielded naphthalene and a very small amount of a liquid hydrocarbon which could not be examined closely.

The entire remaining product of reaction (fraction 182-186°, 83%) was converted into naphthalene on dehydrogenation. The spectrum of the product of reaction in this experiment agreed in its principal frequencies with the spectrum obtained in the first experiment, which pointed to the identity between their composition.

Experiment III was performed at a temperature not exceeding 50°. This was achieved by gradual addition of aluminum chloride to the hydrocarbon and by cooling of the reaction mixture. The reaction product (85% yield), after appropriate purification, was fractionated (Table 1). A low-boiling fraction was absent. The whole reaction product gave naphthalene on dehydrogenation.

TABLE 1

Expt. No.	Temp. of expt. (°C)	Duration of expt.	B.p. of fractions, their yield and properties						
			180-182°				182-184°		
			Yield of reaction product (%)	Content of fraction in reaction products (%)	n_D^{20}	d_4^{20}	Content of fraction in reaction products (%)	n_D^{20}	d_4^{20}
1	100-103	1-1.5 min.	89	–	–	–	3.3	1.4663	0.8643
2	100	15 hrs.	84	6.0	1.4655	0.8624	3.0	1.4660	0.8640
3	40-50	2 hrs.	85	–	–	–	1.5	1.4698	0.8671
4	0	6 hrs.	92	–	–	–	–	–	–

The data of spectrum analysis established that in the conditions of this experiment dicyclopentyl is transformed into decahydronaphthalene, predominantly the trans form.

Experiment IV was carried out for 6 hrs at 0°. The reaction product (89% yield) distilled at 187-189° (756 mm) and had n_D^{20} 1.4700 and d_4^{20} 0.8740. In its spectrum [193 (0); 257 (1); 295 (0); 322 (8; r); 353 (1.5); 373 (1); 397 (0.3); 408 (3); 492 (2.5); 597 (3); 746 (2.5); 754 (1.5); 769 (0); 792 (1.5); 832 (0.7); 846 (2.5); 862 (0.5); 875 (1); 894 (6; r); 932 (0.5); 963 (1; h); 982 (1; h); 1016-1022 (1.5 d); 1040 (2.5); 1055 (2.5); 1070 (1); 1085 (1.5); 1107 (2; r); 1143 (1.5); 1164 (2; r); 1187 (1; h) 1241 (2); 1253 (2); 1268 (2); 1290 (0); 1317 (1.5); 1347 (1.5); 1356 (2); 1388 (0.7); 1443 (10; h); 1465 (0.8)] were detected lines characteristic of dicyclopentyl and cis- and trans-decahydronaphthalenes. Naphthalene was isolated after dehydrogenation.

Isomerization of cyclopentyl-cyclopentanol by dehydration with conc. phosphoric acid 2-Cyclopentyl-cyclopentanol was prepared by hydrogenation of 2-cyclopentyl-cyclopentanone in presence of skeletal nickel at 200° with a hydrogen pressure of about 190 atm.

Heating of 2-cyclopentyl-cyclopentanol with a small quantity of phosphoric acid (s. g. 1.4) on an oil bath at 230-240° gave a hydrogen fraction of unsaturated character which boiled at 70-80° at 13 mm and had n_D^{20} 1.4998; d_4^{20} 0.9006. MR_D 43.72. $C_{10}H_{16}$. Calculated MR_D 43.51. Its hydrogenation over platinized carbon gave a saturated fraction from which was isolated a hydrocarbon with b.p. 186.5-187 (746 mm): n_D^{20} 1.4668; d_4^{20} 0.8665; MR_D 44.17. $C_{10}H_{18}$. Calculated MR_D 43.98. Its dehydrogenation gave a small quantity of naphthalene.

The above data provide convincing evidence of the isomerization of the dicyclopentyl system into the six-membered ring systems of octahydronaphthalene. This observation was confirmed by the measurements of the Raman spectrum.

Spectrum of product of hydrogenation: 257 (1); 299 (1.5); 321 (5); 346 (1); 408 (8); 434 (1); 494 (5); 556 (1), 592 (1.5); 695 (0.5); 746 (1); 753 (4); 792 (1); 832 (1); 845 (3); 862 (1); 875 (2); 893 (6; r); 956 (1); 963 (1) 986 (1.5; r); 1022 (2); 1050 (4); 1065 (1.2); 1100 (1.5; r); 1144 (1.5); 1165 (3); 1183 (1); 1227 (2); 1256 (3.5); 1267 (1), 1318 (1.5); 1347 (1); 1355 (2.5), 1385 (0.5); 1445 (10).

In the spectrum were detected the strongest lines of dicyclopentyl 321, 893, 1022 and 1183, and the intense lines of decahydronaphthalene 408, 494, 592, 845, 1056 and 1256.

SUMMARY

1. The product of isomerization of dicyclopentyl under the influence of aluminum chloride is a mixture of the stereoisomers of decahydronaphthalene in which the trans form predominates.

Change of temperature in the range of 0 to 100° does not influence the nature of the formed hydrocarbons.

2. The isomerization of 2-cyclopentyl-cyclopentanol on dehydration with concentrated phosphoric acid was studied. The reaction product is a mixture of cyclopentylcyclopentene and octahydronaphthalene.

3. The paper [illegible] demonstrated of isomerization of bicyclic compounds of the cyclopentane series with ring expansion to cis- and decahydronaphthalenes

B.p. of fractions, their yield and properties								
184-186°			186-187°			187-189°		
Content of fraction in reaction products (%)	n_D^{20}	d_4^{20}	Content of fraction in reaction products (%)	n_D^{20}	d_4^{20}	Content of fraction in reaction products (%)	n_D^{20}	d_4^{20}
83.1	1.4680	0.8667	5.6	1.4689	0.8690	–	–	–
84.0	1.4693	0.8686	–	–	–	–	–	–
81.8	1.4712	0.8688	14.0	1.4720	0.8720	–	–	–
–	–	–	–	–	–	98.0	1.4700	0.8740

TABLE 2

Hydrocarbon	B.p.	n_D^{20}	d_4^{20}	Author
Dicyclopentyl	188.5-189° (748 mm)	1.4650	0.8659	Prepared in this research
Cis-decahydronaphthalene . .	193.3°	1.4828	0.8980	Ewans [7]
	–	1.48113	0.8976	Seyer [8]
Trans-decahydronaphthalene	185.3	1.4701	0.8720	Ewans [7]
	–	1.46968	0.8700	Seyer [8]
Spirodecane	185-186° (769 mm)	1.4698	0.8766	N. D. Zelinsky and N.V. Elagina [9]

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THERMOCATALYTIC TRANSFORMATIONS OF HYDROCARBONS

I. TRANSFORMATIONS OF PHENYLCYCLOHEXANE

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Our studies of thermocatalytic transformations of aromatic hydrocarbons have shown [1] that the transformation depends on the length of the side chain and the degree of its branching at the carbon atom attached to the aromatic nucleus. In the light of these conclusions it was a matter of interest to investigate the behavior of phenylcyclohexane which contains a radical of considerable size and in which the aromatic ring is attached through a secondary carbon atom.

The synthesis of phenylcyclohexane has been described many times in the literature. It was particularly closely studied by S. S. Nametkin who thought that an analogy might be drawn between polycyclohexylbenzenes and components of petroleum lubricating oils [2]. We accomplished the synthesis of phenylcyclohexane by the action of anhydrous aluminum chloride on a mixture of benzene and chlorocyclohexane in the conditions described by N. I. Kursanov [3]. Chlorocyclohexane was obtained by interaction of cyclohexanol with gaseous hydrogen chloride on refluxing for several hours on a water bath, fresh quantities of hydrogen chloride being introduced from time to time. After heating until the separated layer of water ceased to increase in size, the reaction mixture was washed with water and weak sodium carbonate solution; the product was dried and distilled. The yield of pure chlorocyclohexane was about 75% of the theoretical; it distilled at 141-143°, d_4^{20} 1.0011. Condensation with benzene was performed in presence of 5% of anhydrous aluminum chloride; the reaction proceeded very much less intensively, however, than was reported by N. I. Kursanov and it required heating to 45-50°. The yield of phenylcyclohexane, separated by the usual methods and carefully distilled, was 55%. An additional product was dicyclohexylbenzene with b.p. 238-240°. The latest investigations have shown this to be the para-isomer and not the ortho-isomer as was suggested by N. I. Kursanov [4].

Constants of synthesized phenylcyclohexane: m.p. +6.5°, d_4^{20} 0.9445.

Found %: C 90.12; H 9.95. $C_{12}H_{16}$. Calculated %: C 90.00; H 10.00.

Various authors report d_4^{20} from 0.9436 to 0.9502, m.p. 7°.

The prepared hydrocarbon was subjected to heating with activated gumbrin in a small iron still under a reflux condenser. At the conclusion of the reaction, the mixture was freed from the formed benzene by distillation, and the residue (boiling above 150°) was extracted with ether; removal of the latter left a viscous oil which was added to the previously obtained benzene. The whole mixture was subjected to fractionation in a column.

EXPERIMENTAL

Experiment I. 100 g phenylcyclohexane and 90 g activated gumbrin were placed in a small iron still and the mixture was heated over a burner. In the first few minutes the boiling point of the mixture —determined with a thermometer whose bulb was immersed in the boiling mixture —was 210°. Then the temperature at first fell quickly and after 25 minutes it was steady at 125-130°. At this instant the condenser was moved into the sloping position and the fraction to 150° was distilled off; from the residue was obtained a substance as already described. The whole mixture was distilled, the following fractions being obtained: 1) b.p. 75-85° (12%), d_4^{15} 0.8379; 2) b.p. 85-235° (3%); 3) b.p. 235-245° (39.5%), d_4^{20} 0.9456; 4) b.p. 245-300° (9.5%); 5) b.p. above 300° (29%), d_4^{20} 0.9747. The specific gravity of the 75-85° fraction shows that it is certainly not pure benzene. The 235-245° fraction was considered to be the starting substance; the fraction above 300° partly crystallized and was purified by recrystallization from acetone to form crystals with m.p. 101-102° and molecular weight 240. Elementary analysis revealed 89.31% carbon and 10.93% hydrogen. Since dicyclohexylbenzene requires carbon 89.25% and hydrogen 10.75% with a molecular weight of 242, we are justified in regarding the prepared crystals as p-dicyclohexylbenzene, which had previously been prepared by many authors. However, not more than 10% of the total weight of the fraction boiling above 300° was obtained in the form of crystals.

Experiment II. 120 g phenylcyclohexane and 90 g activated gumbrin were heated in a small still fitted with a short column and a condenser; the volatile fractions were collected as formed, so that throughout the whole reaction period the equilibrium between dicyclohexylbenzene and benzene was being shifted; thus the experimental conditions were more drastic. The duration of the whole experiment was 2½ hours and it was stopped when the temperature in the column was 140°. The products were worked up as before and distilled to give the following fractions (table).

Boiling point (°C)	Yield (in g)	d_{20}^{20}	n_D^{20}
Up to 76	12	0.8169	1.4640
76-78	13	0.8346	1.4723
78-81	8	0.8516	1.4850
81-235	2	—	—
235-245.	31	0.9458	1.5280
245-350 (8 mm) . . .	8	—	—
210-212 (8 mm) . . .	16	0.9798	1.5430
212 (8 mm)	6	0.9800	1.5432
212-248 (8 mm) . . .	4.5	—	1.5450
248-250 (8 mm) . . .	4.5	1.0020	1.5565
Above 250 (8 mm) .	11	—	—
Losses.	4		

Not a single one of the fractions crystallized, even after prolonged cooling to −19°. Elementary analysis of the 212° (8 mm) fraction gave:

Found %: C 89.24; H 10.82. M 238. $C_{18}H_{30}$
Calculated %: C 89.25; H 10.75. M 242.

The refractive index of this fraction and of the adjacent ones was 1.055-1.056, which showed the identity between these fractions. In all respects the 210-212° fractions correspond to the anticipated dicyclohexylbenzene, but the latter was not, however, obtained in the crystalline form.

The 76-81° fractions, with a lower specific gravity than required for benzene, were worked up in the cold with sulfuric acid containing 5% anhydride until the reaction for benzene with formaldehyde was negative. The aniline point of the nonaromatic residue was then determined, also the aniline point of the mixture of the residue with 50% benzene. The results agreed with the aniline point of the original mixture, it being established that the latter also contained about 50% benzene. The nonaromatic residue was subjected to close fractionation to give fractions distilling between 71 and 81°. It was thus shown that the fractions are a mixture of cyclohexane and methylcyclopentane, approximately 50% of each, as evident from the following comparison:

	d_{20}^{20}	n_D^{20}
71-81° fraction	0.7654	1.4184
Pure cyclohexane	0.7815	1.4264
Pure methylcyclopentane . .	0.7502	1.4099
Mixture of 50% cyclohexane + 50% methylcyclopentane . .	0.7658	1.4181

SUMMARY

Even at low temperatures the activated clay gumbrin unusually easily transforms phenylcyclohexane into new products. The normal formation of benzene is accompanied by cleavage of cyclohexane which partially isomerizes to methylcyclopentane. A similar cleavage is known to occur with other benzene homologs containing heavy radicals (for example butylbenzene), but in the case of phenylcyclohexane the phenomenon is exceptionally pronounced. The insignificant yield of p-dicyclohexylbenzene in mild experimental conditions and the complete absence of this hydrocarbon when the reaction takes place in more drastic conditions demonstrate that in place of the anticipated p-dicyclohexylbenzene its isomerization product is formed, namely p-di-(methylcyclopentyl)-benzene, not previously described in the literature. The isomerizing action of activated clays on the cyclohexane ring is known from the literature. What is still uncertain is the degree of purity of the obtained di-(methylcyclopentyl)-benzene, since it is natural to assume that it may contain p-methylcyclopentyl-cyclohexylbenzene, likewise not described in the literature.

Conversion of the yields of products to molar ratios, assuming C_6H_{12} to be a mixture of cyclohexane and methylcyclopentane gives the following values: benzene 2.5, C_6H_{12} 1.3, $C_{18}H_{26}$ 1.0.

Consequently approximately one molecule of phenylcyclohexane splits into benzene and C_6H_{12} and two other molecules into benzene and $C_{18}H_{26}$ i.e., normal disproportionation of radicals proceeds to the extent of 66% and splitting to the extent of 34%.

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THERMOCATALYTIC TRANSFORMATIONS OF HYDROCARBONS

II. TRANSFORMATIONS OF TERT-BUTYLBENZENE

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In a series of investigations by the authors of homologs of benzene, the transformations of methylbenzene, xylene and ethyl- and isopropylbenzenes over activated clay were studied [1]. In the present research a study was made of the behavior of an alkyl benzene in which the radical was linked to the nucleus through a quaternary carbon atom. It could be postulated for example, that tert-butylbenzene would readily undergo transformations similar to the decomposition of tert-butylphenol. Furthermore, radical-disproportionation reactions are known to occur in tertbutylbenzene under the action of anhydrous aluminum chloride. A complete analogy between aluminum chloride and activated clay has been indicated by many authors.

Tert-butylbenzene was synthesized from tert-butyl chloride and benzene with aluminum chloride as catalyst according to the general rules for this type of synthesis. The prepared hydrocarbon boiled at 168-170° and had d_4^{20} 0.8649 and n_D^{20} 1.4919 (the corresponding literature values are 0.8669 and 1.4925).

Thermal catalysis was performed in an iron still with an equal weight of activated gumbrin. From the very start of the experiment the boiling point of the mixture was 130° and after 2 hours the temperature was constant at 120.5°. After working up of the mixture in the usual manner [2], distillation gave the following fractions (see table).

B.p.	Yield (in g)	d_4^{20}	n_D^{20}
79- 85°	11.5	0.8744	1.5000
85-165	1.5	—	—
165-169	38.6	0.8608	1.4321
169-173	0.6	—	—
173-220	8.2	0.8612	1.4897
220-227	6.6	—	—
227-232	9.1	Crystals	—
Residue	3.7		

Elementary analysis of the 227-232° fraction gave: C 88.20% and H 11.80%. The theoretical values for ditert-butylbenzene are %: C 88.34; H 11.66.

Cryoscopic determination of the molecular weight gave (average of four determinations) 181.2 (calcd. 190.1). M.p. 76-77° (in a sealed capillary) (the literature gives 76°).

All these data definitely point to the formation of p-ditert-butylbenzene as a result of the thermocatalytic transformation. Oxidation of this hydrocarbon with potassium permanganate and, in another experiment, with chromic acid mixture did not give any results due in part to the high volatility of the hydrocarbon which sublimed from solutions into the neck of the flask.

The molar ratios between benzene and ditert-butylbenzene are 1.2:1, consequently, rather more benzene than was to be expected had formed; and since the transformation was not accompanied by formation of trisubstituted products, evidently due to steric hindrance, the slight excess of benzene must have been the result of radical cleavage apart from disproportionation.

It is interesting that about 40% of butylbenzene was recovered unchanged, which is considerably less than, for example, in the transformation of ethylbenzene in similar conditions. Only at 300° and with heating of the ethylbenzene for 30 hours in an autoclave is the amount of recovered ethylbenzene about 40%. The far-reaching transformation of tert-butylbenzene at low temperatures is comparable only with the transformation of isopropylbenzene or phenylcyclohexane.

SUMMARY

Substitution of a hydrogen atom in benzene by a radical to the ring through a quaternary carbon atom creates instability of the bond between the radical and the benzene ring, due to which the latter undergoes cleavage with extraordinary ease. Consequently the presence of tert-butylbenzene in petroleum appears highly improbable.

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* See Consultants Bureau Translation, p. 1167.

CONJUGATED SYSTEMS

XLIX. THE PROBLEM OF THE ORDER OF ADDITION OF ALKYL HYPOHALITES TO TERTIARY VINYLACETYLENIC ALCOHOLS

A. A. Petrov, E. S. Bravo, V. V. Davidovich, O. S. Dyatkova and G. V. Kuznetsova

The study of the mutual influence of the double and the triple bond in the reactions of vinylacetylenic compounds with halogens, hydrogen halides and hypohalites offers undoubted interest for the theory of organic chemistry since it throws light on many unsolved problems of the chemistry of unsaturated compounds.

In previous papers it was shown that vinylacetylene adds on bromine at all three possible positions, but the 1,2-product predominates [1]. Hydrogen halides give, depending on the conditions, 1,2- and 1,4-products in various ratios [2-4]. No trustworthy study has hitherto been made of the order of addition of hypohalogen compounds.

Homologs of vinylacetylene with a radical in the 1-position add on bromine [5], and alkyl hypohalites preferentially add on at the double bond (in the 3,4-position). On the other hand with hydrogen halides in presence of Cu_2Hal_2 they give 1,2-products [7].

This variation in the order of addition of halogens, hypohalites and hydrogen halides to α-alkyl-substituted vinylacetylenes calls for thorough investigation and clarification.

We therefore undertook the investigation of the addition of electrophilic agents to other vinylacetylenic compounds and in particular to the readily accessible tertiary vinylacetylenic alcohols. A point of special interest was the establishment of whether addition here took place at the double bond.

In recent years the chemistry of the vinylacetylenic alcohols has been the subject of extensive investigations by I. N. Nazarov [8] and other chemists. On the problem of interest to us however, the literature is entirely lacking in data. In the first place we attempted to determine the order of addition to tertiary vinylacetylenic alcohols of alkyl hypoiodites. The experiments were performed in the usual conditions repeatedly employed by one of us for the synthesis of β-iodoethers [9].

Investigations were made on 9 tertiary alcohols whose formulas are listed in the table.

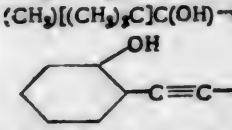
Addition of methylhypoiodite to vinylacetylenic alcohols would be expected to yield 6 substances. Since the reaction products failed to distil without decomposition in the vacuum attainable by us (2 mm), and since we were mainly interested in the tendency of these substances to add on alkyl hypoiodites to the vinyl grouping, we did not isolate the iodoethers but worked up the reaction mixture with alcoholic alkali. In this process, only one of the possible products of addition of alkyl hypohalites to tertiary vinylethinyl carbinols was bound to undergo cleavage with formation of alkoxy derivatives of vinylacetylene (previously studied by one of us [10]) according to the scheme:

$$R_2C(OH)-C\equiv C-CH(OR)-CH_2I \longrightarrow R_2C(OH)-C\equiv C-C(OR)=CH_2 \longrightarrow$$

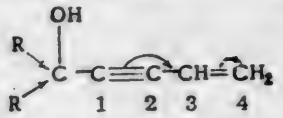
$$\longrightarrow HC\equiv C-C(OR)=CH_2 + R_2C=O.$$

Experiments showed that all the substances enumerated in the table, with exception of 8 and 9, give alkoxyvinylacetylenes as a result of the above-formulated transformations, and accordingly they add on alkyl hypoiodites to a considerable extent at the double bond. The yield of alkoxyvinylacetylenes, and consequently also the relative yield of 3,4-products, increases with the number of radicals in the tertiary alcoholic grouping. Thus, whereas in the case of dimethylvinylethinyl carbinol the yield of methoxyvinylacetylene is 18%, in similar conditions in the case of methyl-tert-butylcarbinol the yield of methoxyvinylacetylene is already 36%. When the radicals are attached to a cyclic system the yield is slightly lowered.

It is possible that these data are evidence of the spatial character of the influence of radicals on the order of addition of alkyl hypoiodites: the complexity of the radical in the 1 position hinders the attack of iodine and thereby favors 3,4-addition. Another possibility is the electronic influence of accumulation of methyl groups in the conjugated

Expt. No.	Starting substance: Formula	Iodoether: Taken (g)	Iodoether: Yield of crude product (in g)	Iodoether: % I: Found	Iodoether: % I: Calc.
1	$(CH_3)_2C(OH)-C\equiv C-CH=CH_2$	55	98.4	44.02	46.99
2	$(CH_3)(C_2H_5)C(OH)-C\equiv C-CH=CH_2$	51	88.3	42.80	44.66
3	$(CH_3)[(CH_3)_3C]C(OH)-C\equiv C-CH=CH_2$	51	80.0	37.53	40.92
4		62	100.0	38.18	41.19
5	$(CH_3)(C_6H_5)C(OH)-C\equiv C-CH=CH_2$	50	85.5	35.82	38.44
6	$(CH_3)(CH_3C_6H_4)C(OH)-C\equiv C-CH=CH_2$	32	45.0	36.46	36.87
7	$(C_6H_5)_2C(OH)-C\equiv C-CH=CH_2$	42	60.0	29.12	32.36
8	$(CH_3)(C_2H_5OC_6H_4)C(OH)-C\equiv C-CH=CH_2$	48	64.0	40.62	33.92
9	$[(CH_3)_2NC_6H_4]_2C(OH)-C\equiv C-CH=CH_2$	50	Not determined		

system: such an accumulation must increase the activity of the vinyl grouping in accordance with the scheme:



Replacement of one alkyl radical by an aryl increases the yield of methoxyvinylacetylene.

The products of interaction of vinylethinylcarbinols 8 and 9 with iodine and mercuric oxide did not give any enynic ether. In place of the latter a small amount of vinylacetylene was obtained. The reason for this may be that the original carbinol was iodinated in the course of the reaction but did not add on alkyl hypoiodite (due to the presence of groups facilitating the entry of halogen into the ring). Other special properties of these alcohols may here come into play, particularly the exceptional susceptibility to dehydration and polymerization under the influence of iodine.

The tertiary alcohol obtained from vinylacetylene and Michler's ketone requires further study; under the action of acid it readily forms a green dye with the vinylacetylenic residue. The yield of enynic ether may be only a relative index of the direction of the reaction. 3,4-Products undoubtedly give enynic ethers not in theoretical amounts under the action of caustic alkalies. Since here we have two stages of reaction and in each stage the yield can hardly exceed 70%, the yield of enynic ether cannot exceed 50%. If this circumstance is taken into consideration, we may conclude that 1,2-addition is nearly always the main direction of the reaction of alkyl hypoiodites with tertiary vinylethinylcarbinols. The ethylenic bond is more reactive than the acetylenic, evidently because of the influence of the radicals in the 1-position. Hydroxyl, however, possibly weakens this influence due to which the addition does not proceed only in the 3,4-position.

EXPERIMENTAL

1. Preparation of Tertiary Vinylacetylenic Alcohols

The first four of the alcohols listed in the table were prepared by A. E. Favorsky's method by the action of powdered alkali on a mixture of vinylacetylene and the appropriate ketone in an ethereal medium. The remaining alcohols were prepared by the Grignard synthesis: the action of the respective ketones on an ethereal solution of vinylethinylmagnesium bromide. The tertiary alcohols prepared from methyl-p-tolyl ketone, methylphenethyl ketone and Michler's ketone are here described for the first time. Their constants are set forth below. The constants of all the other alcohols did not differ substantially from those found by I. N. Nazarov [11], and they are therefore omitted here.

For preparation of methyl-p-tolyl-vinylethinylcarbinol, 45 g methyl-p-tolyl ketone in 100 ml ether was added with cooling and stirring to an ethereal solution of vinylethinylmagnesium bromide prepared from 10 g

Max. yield on I content (in %)	Iodine split off (%)	Yield of methoxyvinylacetylene	Yield of ketone (%)
75.2	81.3	18.0	Not isolated
72.8	88.0	22.1	Not isolated
74.2	89.0	35.9	55
72.9	88.3	19.0	40
75.0	88.3	40.1	57
75.9	96.3	27.1	52
76.7	97.1	26.5	Not isolated
—	98.6	Absent	
		Absent	

magnesium. The following day the mixture was worked up under cooling with ice and saturated ammonium chloride solution. The yield of alcohol was 70%.

Methyl-p-tolyl-vinylethinylcarbinol is a viscous liquid with the odor characteristic of all the alcohols of this series.

B.p. 144-145° at 10 mm, d_4^{20} 1.0043, n_D^{20} 1.5328. MR_D Found 58.88. $C_{13}H_{14}O$. Calculated 57.69.

15.80 mg substance: 48.46 mg CO_2; 10.93 mg H_2O. Found %: C 83.70; H 7.74. $C_{13}H_{14}O$. Calculated %: C 83.83; H 7.58.

By the same method, starting from 37 g crystalline methyl-p-phenethyl ketone, the preparation was carried out of methyl-p-phenethyl-vinylethinylcarbinol in 65% yield. A viscous oil with b.p. 166-169° at 10 mm, d_4^{20} 1.0450, n_D^{20} 1.5503. MR_D Found %: 66.01. $C_{14}H_{16}O_2$. Calculated 63.95.

12.14 mg substance: 34.48 mg CO_2; 8.22 mg H_2O. Found %: C 77.51; H 7.58. $C_{14}H_{16}O_2$. Calculated %: C 77.75; H 7.46.

When preparing the alcohol from Michler's ketone it was necessary to take a considerable quantity of ether for dissolving the ketone. Methyl-p-dimethylaminophenylvinylethinylcarbinol crystallized from ether in the form of a colorless substance, readily changing to green when kept.

2. Action of Iodine and Mercuric Oxide on a Solution of Dimethylvinylethinylcarbinol in Methyl Alcohol*

To a solution of 112 g dimethylvinylethinylcarbinol (30% excess) in 180 ml methanol was added 120 g mercuric oxide; then at 20-25° (water cooling) and with mechanical stirring was introduced 200 g pulverized iodine in small portions over a period of 4 hours. At the conclusion of the reaction, the precipitate of mercuric oxide and mercuric iodide was filtered off and washed on the filter with alcohol; the filtrate was diluted with water. The oil which came down was washed with water and dried with calcium chloride. Yield 185 g of a substance (88% calculated on the iodine) which was treated with alkali without further purification.

185 g of the iodoether was added to a solution (heated on the water bath) of 60 g KOH in 150 ml ethanol, after which the mixture was boiled for another 45 minutes. To the mixture was then added 500 ml water and distillation was carried out in a column. Dilution of the distillate with water caused the methoxyvinylacetylene to separate. The aqueous layer was subjected to a second distillation and a further crop of methoxyvinylacetylene was separated from the first portions. This treatment of the distillates was repeated several times.

The methoxyvinylacetylene was washed twice with conc. calcium chloride solution and distilled in a column. A total of 11.5 g methoxyvinylacetylene was obtained, equivalent to a yield of 20% calculated on the iodoether. Constants found for methoxyvinylacetylene: b.p. 86-87.5°, d_4^{20} 0.8697, n_D^{20} 1.4434. Pure methoxyvinylacetylene prepared by another method [10] had: b.p. 86.5° at 752 mm, d_4^{20} 0.8712, n_D^{20} 1.4446.

3. Action of Iodine and Mercuric Oxide on a Solution of Dimethylvinylethinylcarbinol in Ethyl Alcohol

In the above-described conditions, 66 g dimethylethinylcarbinol (50% excess) in 150 ml ethyl alcohol and 100 g iodine gave 69 g iodoether. Yield 60%. Dehalogenation of this ether gave 7.8 g ethoxyvinylacetylene with b.p. 102-104°, d_4^{20} 0.8541 and n_D^{20} 1.4440. Yield 25%. Constants of pure ethoxyvinylacetylene prepared by another method [10] were: b.p. 103.4-103.7° at 752 mm, d_4^{20} 0.8570, n_D^{20} 1.4432.

* This experiment (and the experiment following) were performed by A. A. Petrov in 1944.

4. Comparative Experiments on the Action of Iodine and Mercuric Oxide in Methanol on Tertiary Vinylethinylcarbinols

To a solution of the vinylethinylcarbinol in an 8-10 fold excess of methanol was added mercuric oxide (50% excess), and, with intensive stirring and at 10-15°, the calculated amount of powdered iodine in small portions. Addition of the iodine required about 1½ - 2 hours. At the conclusion of the reaction the solution was separated from the excess of mercuric oxide and mercuric iodide, and its amount was measured. The amount of iodoether was determined separately on a sample. This was done by diluting the sample with water, extracting the resultant oil with ether, washing the ethereal solution with saturated calcium chloride solution to remove alcohol, and then evaporating the ether in vacuum (2 mm). The residue was weighed and its content of iodine was determined. In some cases the content of methoxyl groups was also determined (Zeisel method). The calculated amounts of iodoethers, based on the iodine and methoxyl group contents, were in good agreement.

Results of analysis of the iodoethers for content of iodine are given in the table. Here we only present the analytical data (Zeisel) for two substances (3 and 5).

For iodoether 3: 0.1762 g substance: 0.1262 g AgI. Found %: CH_3O 9.47. $C_5O_{15}OIOCH_3$. Calculated %: CH_3O 10.01.

For iodoether 5: 0.1826 g substance: 0.1233 g AgI. Found %: CH_3O 8.93. $C_{12}H_{15}OIOCH_3$. Calculated %: CH_3O 9.40.

The main bulk of the solution was worked up with a twofold excess of KOH and separation of methoxyvinylacetylene was effected from the obtained mixture, using the method described in experiment 3; the product was distilled from a small Favorsky flask. The 85-88° fraction was weighed. In the majority of cases the whole of the material distilled over in this range. The iodine ion content of the residue was determined.

The ketones were isolated from the reaction mixture by prolonged steam distillation or by extraction with ether. Their constants corresponded to the literature values. Thus, for example, for pinacoline the values found were: b.p. 103-106°, d_4^{20} 0.8055, n_D^{20} 1.3985. Literature data [12]: b.p. 103-106°, d_4^{16} 0.7999. For acetophenone was found: b.p. 200-202°, d_4^{20} 1.0288; n_D^{20} 1.5522. Literature data [12]: b.p. 202°, d_4^{20} 1.0236, n_D^{20} 1.5342.

The purest preparations of methoxyvinylacetylene were obtained from those carbinols from which are formed ketones nonvolatile in steam, for example from diphenylvinylethinylcarbinol (b.p. 86-87°, d_4^{20} 0.8702, n_D^{20} 1.4440).

SUMMARY

1. An investigation was made of the order of addition of methyl hypoiodite to 9 tertiary dialkyl-, alkylaryl-, and diaryl-vinylethinylcarbinols, as well as of the order of addition of ethyl hypoiodite to dimethylvinylethinylcarbinol.

2. It was established that alkyl hypoiodites add on to a considerable extent in the 3,4-position (at the ethylenic bond).

3. Alkaline cleavage of the reaction products gave methoxy- and ethoxyvinylacetylenes.

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SYNTHESIS OF HYDROCARBONS

XLI. DIISOBUTYLACETYLENE AND DIISOAMYLACETYLENE

R. Ya. Levina, V. V. Ershov and Yu. S. Shabarov

In our preceding communications a new method was described for the synthesis of normal and iso dialkylacetylenes with a central triple bond.

Dialkylacetylenes with a normal structure (I) were synthesized by reaction of organomagnesium compounds with a diprimary acetylenic 1,4-dichloride of the propargyl type – 1,4-dichloro-2-butyne [1,2].

The reaction of methylmagnesium bromide (or iodide) with homologs of 1,4-dichloro-2-butyne (disecondary acetylenic 1,4-dichlorides) was the method used for synthesis of not previously described dialkylacetylenes containing two branched groupings in the α-position to the triple bond: diisopropylacetylene [3], disecondary butylacetylene and disecondary amylacetylene [4]:

$$RCH(CH_3)-C\equiv C-CH(CH_3)R \quad (R = CH_3,\ C_2H_5,\ C_3H_7)$$

In the present research we studied the possibility of employing 1,4-dichloro-2-butyne as the starting material for synthesis of dialkylacetylenes with an iso structure and a central triple bond as well as two branches in the β- and in the γ-position to the triple bond.

It was established that reaction of isopropylmagnesium bromide and isobutylmagnesium bromide with 1,4-dichloro-2-butyne gave, respectively, 2,7-dimethyl-4-octyne (not previously described in the literature) and 2,9-dimethyl-5-decyne* (yield 5% of the theoretical):

$$ClCH_2-C\equiv C-CH_2Cl + 2CH_3CH(CH_3)MgBr \longrightarrow CH_3CH(CH_3)CH_2-C\equiv C-CH_2CH(CH_3)CH_3$$

$$ClCH_2-C\equiv C-CH_2Cl + 2CH_3CH(CH_3)CH_2MgBr \longrightarrow CH_3CH(CH_3)CH_2CH_2-C\equiv C-CH_2CH_2CH(CH_3)CH_3$$

The structure of the prepared alkynes was demonstrated by oxidation to the corresponding acids – isovalenic and isocaproic acids (identified by the melting points of the anilides).

The simplicity of the synthesis (in the usual conditions of the Grignard reaction) and the fewness of the stages permit this method to be recommended for preparation of the previously inaccessible dialkylacetylenes with an iso structure, a central triple bond and two branched (methyl) groups at various distances from the triple bond. The yields of these hydrocarbons, however, are low.

Comparison of the physical properties of the dialkylacetylenes synthesized by us in the present and the preceding [1-4] researches showed that these compounds are characterized by exaltation of molecular refraction on transition from hydrocarbons with a normal structure to those which are symmetrically branched, as well as on progressive approach of both branches to the triple bond (Table 1).

When performing the reactions between isopropyl- and isobutylmagnesium bromides and dichlorobutyne, the processes that took place were similar to those observed by us in preceding investigations [2,4]. Thus, on fractionation in a column of the products of both reactions, separation was effected of the conjugated dienic hydrocarbons (not described in the literature): 2,3-diisopropyl-1,3-butadiene and 2,3-diisobutyl-1,3-butadiene (yield

* From the product of reaction between acetylene dimagnesium bromide and isoamylbromide M. S. Malinovsky [5] isolated, 2,9-dimethyl-6-decyne, which distilled over the range of 200-212°.

TABLE 1

Exaltation of Molecular Refraction of Dialkylacetylenes

Branch	Formula	Name	EM_D^*	Literature references
None	$C_2H_5-C\equiv C-C_2H_5$	3-Hexyne(diethylacetylene)	0.21	[1]
	$C_3H_7-C\equiv C-C_3H_7$	4-Octyne(dipropylacetylene)	0.42	[2]
	$C_4H_9-C\equiv C-C_4H_9$	5-Decyne(dibutylacetylene)	0.39	[2]
	$C_5H_{11}-C\equiv C-C_5H_{11}$	6-Dodecyne(diamylacetylene)	0.41	[2]
In the γ-position to the triple bond	$CH_3CHCH_2CH_2-C\equiv C-CH_2CH_2CHCH_3$ (CH₃ at each end)	2,9-Dimethyl-5-decyne-(diisoamylacetylene)	0.55	Prepared in this research
In the β-position to the triple bond	$CH_3CHCH_2-C\equiv C-CH_2CHCH_3$ (CH₃ at each end)	2,7-Dimethyl-4-octyne-(diisobutylacetylene).	0.76	Prepared in this research
In the α-position to the triple bond	$CH_3CH-C\equiv C-CHCH_3$ (CH₃ at each end)	2,5-Dimethyl-3-hexyne-(diisopropylacetylene)	0.92	[3,4]
	$C_2H_5CH-C\equiv C-CHC_2H_5$ (CH₃ at each end)	3,6-Dimethyl-4-octyne-(disec-butylacetylene)	0.92	[4]
	$C_3H_7CH-C\equiv C-CHC_3H_7$ (CH₃ at each end)	4,7-Dimethyl-5-decyne-(disec-amylacetylene)	1.04	[4]

5-6% of the theoretical), whose formation is explained by a twofold allylic rearrangement of the dichlorobutyne in the instant of reaction [1]:

$$ClCH_2-C\equiv C-CH_2Cl \xrightarrow{2\,RMgBr} CH_2=\underset{R}{C}-\underset{R}{C}=CH_2$$

R = C_3H_7-iso and C_4H_9-iso

The isolated dienic hydrocarbons were characterized by the preparation of crystalline adducts with maleic anhydride [6].

In comparison with many conjugated dienic hydrocarbons, 2,3-diisopropyl-1,3-butadiene and 2,3-diisobutyl-1,3-butadiene have lower constants and a considerably lower exaltation of molecular refraction than those characterizing homologs of 1,3-butadiene with free methylene groups at the ends of the conjugated system: $(CH_2=C(R)-CH=CH_2$ and $CH_2=C(R)-C(R)=CH_2)$.

TABLE 2

Dienic hydrocarbons	EM_D	
	R = CH_3	R = C_3H_7-iso
$R-CH=CH-CH=CH_2$	1.55 [7]	1.81 [8]
$CH_2=C(R)-CH=CH_2$	1.00 [7]	0.69 [8]
$CH_2=C(R)-C(R)=CH_2$	0.77 [10]	0.26 (our research)

Table 2 contains some examples illustrative of this characteristic change of exaltation of molecular refraction of conjugated dienes in dependence on the position of the alkyl groups.

A second side reaction — the formation of alkanes from radicals of organomagnesium compounds under the action of 1,4-dichloro-2-butyne —

$$ClCH_2-C\equiv C-CH_2Cl + 2RMgBr \longrightarrow R-R + 2MgBrCl + (-CH_2C\equiv C-CH_2-)x,$$ where R = C_3H_7-iso and C_4H_9-iso.

* The molar refractions were calculated by the usual method: summation of the atomic refractions and the increment of the triple bond.

gave lower yields (5 and 10% of the theoretical) of the respective alkanes (R—R) than when using unbranched alkylmagnesium halides [2].

EXPERIMENTAL

Synthesis of Diisobutylacetylene (2,7-Dimethyl-4-octyne)

To isopropylmagnesium bromide (105 g isopropyl bromide, 20 g magnesium and 225 ml absolute ether) was slowly added, with continual stirring and periodic cooling with water, an ethereal solution (1:1 by volume) of 1,4-dichloro-2-butyne (b.p. 75° at 28 mm; 41 g; 1/3 mole). The reaction mixture was stirred for a further 3 hours at room temperature; decomposition was effected on the following day with dilute 2 N acetic acid. Another four experiments were carried out in similar conditions. The ether was distilled off from the washed and dried ethereal extracts and the residue distilled to give two broad cuts with b.p. 42-70° (761 mm) and 44-80° (25 mm).

The 42-70° fraction was freed from traces of halide by treatment with sodium in liquid ammonia; it was then distilled in a column (50 theoretical plates) to give 5 g (5% of the theoretical reckoned on the 1,4-dichloro-2-butyne) 2,3-dimethylbutane (diisopropyl): b.p. 56.5-57° (755 mm); n_D^{20} 1.3755; d_4^{20} 0.6595.

Literature data: b.p. 57.9° (760 mm); n_D^{20} 1.3722; d_4^{20} 0.6615 [11].

The 44-80° (25 mm) fraction was heated with sodium and distilled over sodium. It was then fractionally distilled in a column (50 theoretical plates) to give two isomeric hydrocarbons: 2,3-diisopropylbutadiene-1,3 (9.5 g, 5.5% of the theoretical) and 2,7-dimethyl-4-octyne (8 g, 5% of the theoretical, reckoned on the dichlorobutyne).

2,3-Diisopropyl-1,3-butadiene (not described in the literature):

B.p. 145.5-146° (744 mm), n_D^{20} 1.4400, d_4^{20} 0.7639; MR_D 47.70; $C_{10}H_{18}F_2$. Calculated: MR_D 47.44; EM_D 0.26.

Found %: C 86.68, 86.77; H 13.30, 13.22. $C_{10}H_{18}$. Calculated %: C 86.94; H 13.06.

2,3-Diisopropylbutadiene readily entered into reaction with maleic anhydride (on brief heating without a solvent); the adduct had m.p. 118°, and its analysis corresponded to the composition $C_{14}H_{18}O_3$.

Found %: C 71.10, 70.99; H 8.62, 8.51. Calculated %: C 71.14; H 8.32.

2,7-Dimethyl-4-octyne (diisobutylacetylene; not described in the literature):

B.p. 158-158.5° (748 mm), n_D^{20} 1.4328; d_4^{20} 0.7619; MR_D 47.11; $C_{12}H_{22}F_2$. Calculated: MR_D 46.38; EM_D 0.76.

Found %: C 86.96, 86.79; H 13.24, 13.26. $C_{12}H_{22}$. Calculated %: C 86.94; H 13.06.

Oxidation of the isolated 2,7-dimethyl-4-octyne (5.4 g) with 68% nitric acid (9 ml) in presence of mercuric nitrate (0.2 g) led to formation of only isovaleric acid with b.p. 175-178° at 757 mm (2.7 g, 33.7% of the theoretical); m.p. of the anilide 116°; a mixed melting test with the anilide of authentic isovaleric acid did not give a depression of melting point.

Literature data for isovaleric acid [12]: b.p. 176° (760 mm); anilide, m.p. 109°.

Synthesis of Diisoamylacetylene (2,9-Dimethyl-5-decyne)

The reaction between isobutylmagnesium bromide (20 g magnesium, 125 g isobutyl bromide and 225 ml absolute ether) and 1,4-dichloro-2-butyne (41 g, 1/3 mole) was performed by the above described procedure. Vacuum distillation of the product of reaction (from five experiments) gave two broad fractions: 1) b.p. 40-80° (145 mm) and 2) b.p. 50-100° (25 mm).

The lower boiling fraction was freed from traces of halide by the action of sodium in liquid ammonia; distillation in a column with 50 theoretical plates gave 16 g (10% of the theoretical reckoned on the dichlorobutyne) 2,5-dimethylhexane:

B.p. 107.8-108° (751 mm), n_D^{20} 1.3940; d_4^{20} 0.6981.

Literature data [13]: b.p. 109.3° (760 mm); n_D^{20} 1.3930; d_4^{20} 0.6949.

The 50-100° (25 mm) fraction was vacuum-fractionated in a column to give 2,3-diisobutyl-1,3-butadiene (10.4 g, 4.2% of the theoretical) and 2,9-dimethyl-5-decyne (12.5 g, 5% of the theoretical calculated on the initial dichlorobutyne).

2,3-Diisobutyl-1,3-butadiene (not described in the literature):

B.p. 75° (19 mm); n_D^{20} 1.4452; d_4^{20} 0.7736; MR_D 57.14. $C_{12}H_{22}$. Calculated: MR_D 56.68; EM_D 0.46.

Found %: C 86.49, 86.68; H 13.44, 13.24. $C_{12}H_{22}$. Calculated %: C 86.66; H 13.34.

2,3-Diisobutylbutadiene reacts readily with maleic anhydride (under the same conditions as in the case of 2,3-diisopropylbutadiene-1,3). The adduct has melting point 64°, its analysis corresponding to $C_{16}H_{24}O_3$.

Found %: C 72.81, 72.65; H 9.09, 9.23. $C_{16}H_{24}O_3$. Calculated %: C 72.69; H 9.15.

2,9-Dimethyl-5-decyne (diisoamylacetylene): b.p. 91.9° (19 mm); n_D^{20} 1.4398; d_4^{20} 0.7814; MR_D 56.16. $C_{12}H_{22}$. Calculated MR_D 55.61; EM_D 0.55.

Found %: C 86.83, 86.79; H 13.22, 13.27. $C_{12}H_{22}$. Calculated %: C 86.66; H 13.34.

Literature data [5]: b.p. 200-212°; n_D^{20} 1.4315; d_4^{17} 0.795.

Oxidation of 2,9-dimethyl-5-decyne (3.6 g) in the conditions outlined above gave only isocaproic acid with b.p. 192-194° at 760 mm (1.5 g, 30% of the theoretical). The anilide melts at 112°. The anilide which we specially synthesized from isocaproic acid had m.p. 111°; m.p. of mixed specimen 111-112°.

Literature Data for isocaproic acid [12]: b.p. 195°, anilide, m.p. 111°.

The structure of 2,9-dimethyl-5-decyne and 2,7-dimethyl-4-octyne was confirmed by the presence of the characteristic frequencies of the triple bond in their Raman spectra. This optical investigation* also showed that the alkynes synthesized by us did not contain admixtures of alkenes or alkadienes.

SUMMARY

1. A study was made of the reaction between 1,4-dichlorobutyne and alkylmagnesium bromides containing a branched radical — isopropyl — and isobutylmagnesium bromides.

2. It was shown that the reaction proceeds in three directions: with formation of dialkylacetylenes with a symmetrically branched structure (normal reaction products), 2,3-dialkyl-1,3-butadiene (resulting from a twofold allylic rearrangement of the initial dichlorobutyne in the instant of reaction), and alkanes (formed by dimerization of the radicals of the organomagnesium compound).

3. Products synthesized for the first time were 2,3-diisopropylbutadiene-1,3, 2,3-diisobutyl-1,3-butadiene, 2,7-dimethyl-4-octyne (diisobutylacetylene). 2,9-Dimethyl-5-decyne- (diisoamylacetylene) was obtained with more accurate constants than those reported in the literature.

4. The structure of 2,7-dimethyl-4-octyne and 2,9-dimethyl-5-decyne was confirmed by their oxidation to isovaleric and isocaproic acids, which were characterized as their crystalline anilides.

5. The structure of both the diene hydrocarbons was confirmed by the preparation of the products of their addition to maleic anhydride (not described in the literature).

6. It was shown that the exaltations of the molecular refractions of symmetrical acetylenic hydrocarbons with a central triple bond increase on transition from hydrocarbons with a normal structure to those with symmetrical branches and on approach of both branches to the triple bond.

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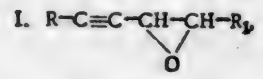
OXIDATION OF VINYLACETYLENIC HYDROCARBONS BY ORGANIC HYDROPEROXIDES

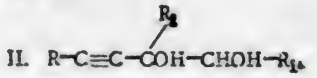
1. OXIDATION OF 4-PHENYLETHINYL-3-HEPTENE BY ACETYL HYDROPEROXIDE

N. M. Malenok and I. V. Sologub

It has been established that the oxidation of vinylacetylenic hydrocarbons of various structures by acetyl hydroperoxide proceeds at the double bond with formation of acetylenic oxides (I) [1-4]:



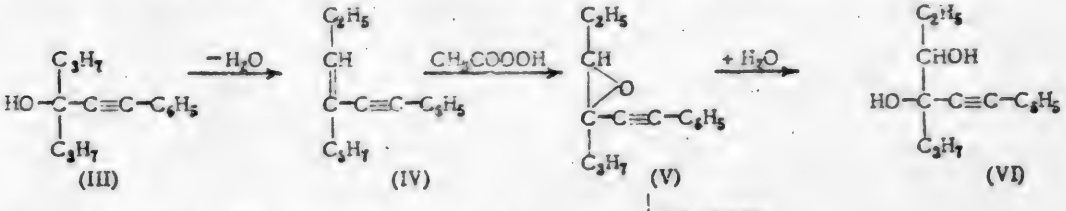
but sometimes glycols (II) and mono- and diacetates of unsaturated hydrocarbons are obtained [5, 6]; these are secondary products formed from the oxides:



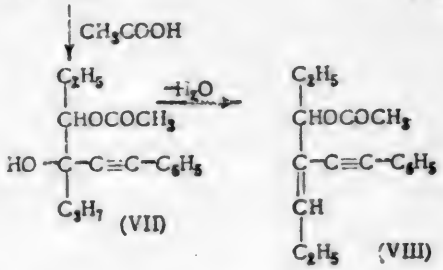
Similar results were obtained by other authors [7, 8, 9, 10] on oxidation of various unsaturated hydrocarbons with organic hydroperoxides.

When the oxide ring is formed with two secondary carbon atoms, the resultant acetylenic oxide is stable and can be easily isolated; but an oxide ring with a secondary and a tertiary carbon atom is unstable and in the process of formation and separation it readily undergoes acetylation and hydration.

In the present research we aimed at confirming this behavior by oxidizing (with acetyl hydroperoxide) a vinylacetylenic hydrocarbon – 4-phenylethinyl-3-heptene (IV) – whose structure differed from that of the previously oxidized unsaturated hydrocarbons. The starting substance for this hydrocarbon was the acetylenic alcohol 4-phenylethinyl-heptan-4-ol (III) which was prepared by Zh. I. Iotsich's method from phenylacetylene and dipropyl ketone. The alcohol was then dehydrated with acetic anhydride to form the unsaturated hydrocarbon. Its oxidation with acetyl hydroperoxide led to isolation of three products: an oxide, 4-phenylethinyl-3-heptene (V); an acetylenic glycol, 4-phenylethinylheptane-3, 4-diol (VI); and a vinylacetylenic monoacetate, 4-phenylethinyl-5-acetylhydroxy-3-heptene (VIII):



(III) (IV) (V) (VI)



(VII) (VIII)

Formation of these compounds proceeds in the following manner. Oxidation of 4-phenylethinyl-3-heptene (IV) with acetyl hydroperoxide at first gives the oxide (V), which with acetic acid forms the monoacetate of alcohol (VII) (not isolated by us); the latter undergoes dehydration to form the vinylacetylenic monoacetate (VIII). At the same time the acetylenic oxide (V) also undergoes some dehydration with formation of the glycol (VI) in which the presence of the triple bond was demonstrated by quantitative bromination.

EXPERIMENTAL

Synthesis of 4-Phenylethinylheptan-4-ol

100 g phenylacetylene (b.p. 143-145° at 738 mm) was condensed by the Iotsich reaction with 111 g dipropyl ketone (b.p. 140-142° at 744 mm); a liquid mass was obtained, from which three fractional distillations yielded 140 g light-yellow liquid with b.p. 119-120° at 0.5 mm. Yield 66.1%, reckoned on the phenylacetylene.

d_{4}^{20} 0.9487; n_D^{20} 1.5330; MR_D 70.69; calculated 67.39.

0.1194 g substance: 0.3663 g CO_2; 0.1058 g H_2O. 0.1238 g substance: 0.3800 g CO_2; 0.1062 g H_2O. 0.1142 g substance: 12.25 ml CH_4 (18.5°, 737.5 mm). 0.3499 g substance; 27.75 g C_6H_6; Δt 0.31°. Found %: C 83.67, 83.69; H 9.84, 9.53; OH 7.4; M 209.0. $C_{15}H_{20}O$. Calculated %: C 83.27; H 9.33; OH 7.9; M 216.1.

The prepared alcohol dissolved readily in ethyl alcohol, ethyl ether, chloroform and benzene. Insoluble in water.

Dehydration of 4-Phenylethinylheptan-4-ol with Acetic Anhydride

129 g of the alcohol was mixed with 280 ml acetic anhydride. The mixture was refluxed in a flask for 8 hours. The excess of acetic anhydride and the formed acetic acid were distilled off; three fractional distillations of the residual mass gave a light-yellow liquid with b.p. 110-112°(0.5 mm). Yield 98 g (82.6%); d_{4}^{20} 0.9049; n_D^{20} 1.5540.

0.1223 g substance: 0.4076 g CO_2; 0.1091 g H_2O. 0.1393 g substance: 0.4636 g CO_2; 0.1165 g H_2O. 0.2794 g substance; 23.26 g C_6H_6: Δt 0.32°. Found %: C 90.89, 90.77; H 9.91, 9.29; M 192.6. $C_{15}H_{18}$. Calculated %: C 90.86; H 9.14; M 198.1.

The prepared vinylacetylenic hydrocarbon — 4-phenylethinyl-3-heptene — had good solubility in the above-mentioned solvents, just like the alcohol. It did not exhibit any appreciable polymerization after standing for 7 months.

Oxidation of 4-Phenylethinyl-3-heptene with Acetyl Hydroperoxide

33.5 g of the vinylacetylenic hydrocarbon was oxidized in a medium of absolute ethyl ether at a temperature of +2° with 26 g of 69.1% acetyl hydroperoxide.

The reaction proceeded with insignificant rise of temperature to +4°. After addition to the hydrocarbon of the whole of the acetyl hydroperoxide, the mixture was allowed to stand at room temperature. The completion of the reaction was checked by withdrawing a 1 ml sample every 2 days, diluting it with water to 100 ml and titrating with 0.1 N thiosulfate. In this way it was established that the reaction of oxidation of 4-phenylethinyl-3-heptene with acetyl hydroperoxide took place over a period of 10 days, the concentration of hydroperoxide being found unchanged after further titration.

The nonreacted acetyl hydroperoxide and the formed acetic acid were removed by washing twice with water and once with 2% sodium carbonate solution. The ethereal layer containing the oxidation products was separated, dried with potassium carbonate for 24 hours and filtered. The ether was driven off and the residue fractionated in vacuum. Three fractionations gave the following:

1) b.p. 128-129° (0.5 mm), 1.9 g; 2) b.p. 156-159° (0.5 mm), 8 g; 3) b.p. 147-148° (2mm), 6.5 g.

Examination of substance with b.p. 128-129° (0.5 mm). This was a light-yellow liquid, soluble in ethyl ether, ethyl alcohol and chloroform; d_4^{20} 0.9743; n_D^{20} 1.5360.

0.1367 g substance: 0.4186 g CO_2; 0.1024 g H_2O. 0.1325 g substance: 0.4070 g CO_2; 0.0999 g H_2O. Found %: C 83.71, 83.77; H 8.32, 8.38. $C_{15}H_{18}O$. Calculated %: C 84.10; H 8.46.

The analytical data show that the substance is 4-phenylethinylheptene-3.

Examination of substance with b.p. 156-159° (0.5 mm). After fractional distillation it consisted of a viscous yellow liquid which crystallized on standing in the form of slender, white crystals with m.p. 108-109°.

0.1193 g substance: 0.3385 g CO_2; 0.0950 g H_2O. 0.1146 g substance: 0.3257 g CO_2; 0.0921 g H_2O. 0.1180 g substance: 25.70 ml CH_4 (18.5°, 738 mm). Found %: C 77.38, 77.51; H 8.85, 8.93; OH 15.02. $C_{15}H_{22}O_2$. Calculated %: C 77.55; H 8.66; OH 14.65.

The experimental data indicate that the substance is the acetylenic glycol, 4-phenylethinylheptane-3, 4-diol which dissolves in ethyl ether, ethyl alcohol, methyl alcohol and chloroform and is insoluble in water.

The presence of a triple bond in the glycol was shown by quantitative bromination. 0.2029 g substance, dissolved in chloroform, added on 0.3050 g bromine, which is the theoretical amount for addition of four bromine atoms or 0.2797 g for one triple bond.

Examination of substance with b.p. 147-148° (2 mm). Yellow liquid, soluble in the same solvents as the acetylenic glycol.

d_4^{25} 1.0100; n_D^{25} 1.5312; MR_D 76.94; calculated 76.19.

0.1103 g substance: 0.3223 g CO_2; 0.0792 g H_2O. 0.1041 g substance: 0.3045 g CO_2; 0.0765 g H_2O. Found %: C 79.69, 79.77; H 7.98, 8.17. $C_{27}H_{28}O_2$. Calculated %: C 79.65; H 7.85.

The data show that the substance is the monoacetate of the vinylacetylenic hydrocarbon, 4-phenylethinyl-5-acetylhydroxy-3-heptene.

SUMMARY

1. The tertiary acetylenic alcohol, 4-phenylethinylheptan-4-ol, was synthesized and converted by acetic anhydride dehydration into the vinylacetylenic hydrocarbon, 4-phenylethinyl-3-heptene.

2. Oxidation of 4-phenylethinyl-3-heptene with acetyl hydroperoxide gave its oxide, also an acetylenic glycol — 4-phenylethinylheptane-3,4-diol — and a vinylacetylenic monoacetate — 4-phenylethinyl-5-acetylhydroxy-3-heptene; these are products of secondary reactions involving the oxide.

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SULFONATION AND SULFONIC ACIDS OF ACIDOPHOBIC COMPOUNDS

XXIV. SULFONATION OF ISOBUTENE AND TRIMETHYLETHYLENE

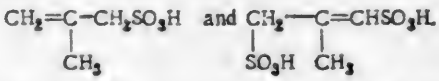
A. P. Terentyev, A. V. Dombrovsky and R. A. Gracheva

In 1947 A. P. Terentyev, in his paper on "Sulfonation and sulfonic acids of acidophobic compounds" [1] showed, on the basis of considerable experimental material, that pyridine-sulfotrioxide is a good sulfonating medium for substances which are easily modified by the action of acidic reagents. Sulfonation with this agent gives good yields of unsaturated sulfonic acids which possess well-marked activity at the double bond [2]. The activity of the double bond in isobutene and trimethylethylene is brought about by the positive inductive effect of the methyl groups which are unsymmetrically distributed at the double bond. Both these hydrocarbons possess great reactivity, and a large number of their chemical reactions have been studied including substitution of hydrogen atoms by various groups.

On treatment with sulfuric acid, isobutene and trimethylethylene undergo a whole series of complex transformations, mainly involving polymerization, hydration and resinification.

A. M. Butlerov [3] studied the polymerization of isobutene under the action of sulfuric acid. S. V. Lebedev and G. G. Koblyansky [4] later studied the polymerization of isobutene by Butlerov's method and obtained a complex mixture of products.

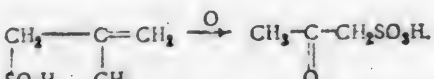
In 1941 Suter and co-workers [5] studied the action of dioxane-sulfotrioxide on isobutene. On passing the latter into a suspension of dioxane-sulfotrioxide in dichloroethane, they isolated a mixture of two sulfonic acids:



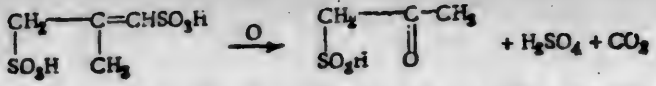
Nothing about the sulfonation of trimethylethylene has appeared in the literature.

We attempted the sulfonation of isobutene and trimethylethylene under pressure, a mixture of a 50% solution of the hydrocarbons in dichloroethane and pyridine-sulfotrioxide being heated to 100-110°. The reaction mass was worked up to yield a mixture of the barium salts of the unsaturated sulfonic acids. It ought to be noted that the agent used in the reaction was the so-called "acid" pyridine-sulfotrioxide (containing 0.5% free sulfur trioxide). In both cases the mixture consisted of mono- and disulfonic acids.

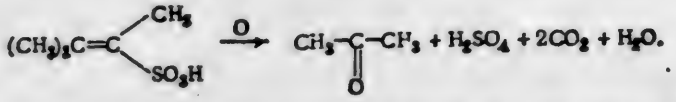
2-Methylpropene-1 (isobutene). The yield of sulfonic acids was about 50%. Separation of the acids in the mixture was facilitated by the differing solubilities of their sodium salts in absolute ethyl alcohol. The structure of the obtained products was verified by oxidation. Rapid discoloration occurred when a salt of the monosulfonic acid was treated with potassium permanganate, but the sulfo group was not split off even after prolonged heating with the oxidizing agent. No acetone was detected among the reaction products. From the filtrate after oxidation was isolated a salt whose composition corresponded to acetonesulfonic acid. Consequently, the monosulfonic acid corresponded in structure to 2-methylpropene-3 sulfonic acid, oxidation of which proceeded according to the scheme:



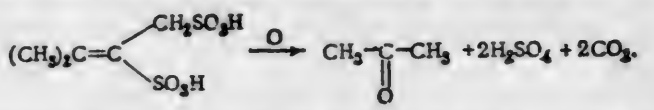
When permanganate reacts with the salt of the disulfonic acid, one-half of the sulfur is split off in the form of sulfate ion; it is clear that one sulfo group is located at the double bond. The salt of acetonesulfonic acid was found among the oxidation products. Consequently, the disulfonic acid has the structure of 2-methyl-propene-1, 3-disulfonic acid. Its oxidation proceeds according to the scheme:



2-Methylbutene-2 (trimethylethylene). Sulfonation of trimethylethylene gave a mixture of mono- and disulfonic acids in a total yield of 54.5%. The components were separated by reprecipitation of the saturated aqueous solutions of the barium salts with methyl alcohol. This treatment brings down the salt of the monosulfonic acid. Salts (K, Na, Ba) of the monosulfonic acid are quicklyoxidized by permanganate solution, in which process the sulfo group is completely detached in the form of sulfate ion; acetone was detected among the reaction products. Consequently, the sulfonic acid had the structure of 2-methylbutene-2-sulfonic acid-3 whose oxidation proceeded according to the scheme:



Oxidation of the salt of the disulfonic acid in similar conditions showed that the whole of the sulfur is likewise split off in the form of sulfate ion; acetone was again found in the oxidation products. Consequently this acid corresponds to 2-methylbutene-2-disulfonic acid-3,4 which is decomposed as follows on oxidation:



The free sulfonic acids, obtained by precipitation of the barium salts with sulfuric acid solution, are only stable in the form of solutions whose concentration does not exceed 75-80%. On further concentration they decompose with separation of sulfuric acid and resinous bodies.

EXPERIMENTAL

I. Sulfonation of 2-Methylpropene-1 (isobutene).

Isobutene was prepared by dehydration of isobutyl alcohol or by passing the latter over alumina at 300°. The gas was dried by passage over calcium chloride and was condensed in a receiver immersed in a freezing mixture.

46 g (0.284 mole) pyridine-sulfotrioxide and a solution of 8 g (0.142 mole) isobutene in 12.6 ml dichloroethane were heated in a stainless steel autoclave of 500 ml capacity for 10 hours at 100-110°. When the autoclave was opened the unreacted isobutene escaped; there was no sulfur dioxide. The sulfonation product, a viscous mass, deliquescing in the air, was dissolved in water and treated with concentrated ammonia. The aqueous-ammoniacal layer was separated and washed several times with benzene to remove the pyridine; it was then treated with excess of barytes and evaporated to dryness. The dry residue was dissolved in water; the excess of barytes was precipitated with carbon dioxide. The filtrate, containing the barium salts of the sulfonic acids, was evaporated on a water bath. Water was removed from the salt by boiling with benzene. Yield 18 g white crystalline salt whose aqueous solutions were decolorized by bromine water and potassium permanganate.

5.707 mg substance: 3.425 mg $BaSO_4$. 3.714 mg substance: 2.257 mg $BaSO_4$. Found %: Ba 35.31, 35.76. $(C_4H_7O_3S)_2Ba$. Calculated %: Ba 33.69. $C_4H_6O_6S_2Ba$. Calculated %: Ba 39.07

The analysis shows that a mixture of mono- and disulfonic acids was obtained. For the purpose of separating these, their barium salts were converted into sodium salts by addition of the equivalent amount of sodium sulfate. The filtrate was evaporated to dryness and the salt dried by boiling with benzene. 10 g of the obtained sodium salt was placed in an extractor for extraction with boiling alcohol. Extraction with 150 ml hot absolute alcohol for 32 hours yielded 3.1 g sodium salt whose composition corresponded to the monosulfonic acid.

3.893 mg substance: 1.720 mg Na_2SO_4. Found %: Na 14.64. $C_4H_7O_3SNa$. Calculated %: Na 14.54.

The insoluble portion contained 6.5 g salt whose sodium content corresponded to the disulfonic acid.

5.770 mg substance: 3.055 mg Na_2SO_4. Found %. Na 17.14. $C_4H_6O_6S_2Na_2$. Calculated %: Na 17.68.

Oxidation of the sodium salt of the monosulfonic acid. To 1.5 g salt in 30 ml water was added in small portions with frequent shaking, 3 g finely pulverized potassium permanganate. After 4 hours' heating decolorization had taken place. The filtrate was evaporated to a small volume and worked up with barium chloride solution. The resultant white precipitate, after treatment with dilute acetic acid solution, was dissolved in hot water and the

filtrate was evaporated. The resultant crystals of barium salt were recrystallized from hot water. The analysis corresponded to acetonesulfonic acid.

8.778 mg substance: 4.986 mg $BaSO_4$. Found %: Ba 33.42. $(C_3H_5O_4S)_2Ba$. Calculated %: Ba 33.40.

Oxidation of the sodium salt of the disulfonic acid. 2.5 g salt was oxidized with 5 g potassium permanganate. The filtrate was treated with barium chloride. The precipitate of barium sulfate weighed 2.29 g which corresponded to cleavage of one sulfo group. The filtrate also contained the barium salt of acetonesulfonic acid.

II. Sulfonation of 2-Methylbutene-2 (Trimethylethylene)

Trimethylethylene was prepared by the N. D. Zelinsky reaction by the procedure described by S. G. Krapivin [6] (heating of isoamyl alcohol with anhydrous oxalic acid). Constants of the prepared hydrocarbon: b.p. 35.5°, d_4^{20} 0.6647, n_D^{17} 1.3888, in accord with the literature.

7 g (0.1 mole) trimethylethylene in 10.5 ml dichloroethane was sulfonated with 32 g (0.2 mole) pyridine-sulfotrioxide by the same procedure as for isobutene. Working up in the appropriate manner led to isolation of 21.5 g barium salts.

6.261 mg substance: 3.765 mg $BaSO_4$. Found %: Ba 35.34. $(C_5H_9O_5S)_2Ba$. Calculated %: Ba 31.52. $C_5H_8O_6S_2Ba$. Calculated %: Ba 37.57.

Separation of the individual salts. A saturated aqueous solution of 10 g barium salt was precipitated with methyl alcohol. The salt of the monosulfonic acid came down. After 3 reprecipitations, two salt fractions were isolated: 1) 4 g, corresponding to the monosulfonic acid, and 2) 6 g, corresponding to disulfonic acid.

Barium determination in the salt of the monosulfonic acid:

10 mg substance: 5.413 mg $BaSO_4$. Found %: Ba 31.53. $(C_5H_9O_5S)_2Ba$. Calculated %: Ba 31.52.

Barium determination in the salt of the disulfonic acid:

8.085 mg substance: 5.134 mg $BaSO_4$. Found %: Ba 37.80. $C_5H_8O_6S_2Ba$. Calculated %: Ba 37.57.

Oxidation of the salt of the monosulfonic acid. 2 g salt in 20 ml water was oxidized by addition of 5.5 g finely pulverized potassium permanganate. At the conclusion of the reaction, a few milliliters was distilled off and tested for acetone by adding alkali followed by iodine in potassium iodide; the characteristic crystals of iodoform were precipitated. Barium ions were not detected in the filtrate. Barium sulfate was isolated from the precipitate, after dissolution of the manganese dioxide.

Oxidation of the barium salt of the disulfonic acid. 2 g barium salt of the disulfonic acid was oxidized in the same conditions as in the preceding case. Barium sulfate was found in the precipitate after working up with hydrochloric acid. The filtrate was treated with barium chloride to give 1.2 g barium sulfate, which corresponds to the second sulfo group. In the filtrate, after oxidation, acetone was detected by the iodoform reaction.

SUMMARY

1. Pyridine-sulfotrioxide was used for sulfonation of isobutene and trimethylethylene. In both cases a mixture of mono- and disulfonic acids was obtained.

2. Resolution of the mixture of sulfonic acids was accomplished by fractional crystallization of their salts. The structure of the acids was demonstrated by oxidation with $KMnO_4$.

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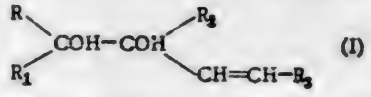
SYNTHESIS AND TRANSFORMATION OF α-GLYCOLS OF THE OLEFINIC SERIES

I. PREPARATION OF 2-METHYL-3,5-DIPHENYLPENTENE-4-DIOL-2,3

L. F. Chelpanova and Z. V. Printseva

In spite of the numerous investigations in the field of glycols of the olefinic series, the synthesis and transformation of disecondary olefinic α-glycols (pinacones) of the type of (I) have hardly been studied.



(I)

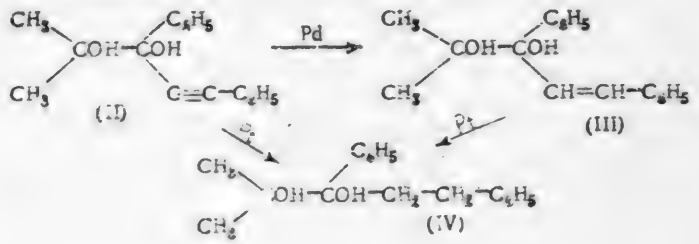
We set out to investigate the transformations of this type of compound in the presence of acid catalysts, selecting in the first instance 2-methyl-3,5-diphenylpentene-4-diol-2,3 (II) as the object of study.

In this paper we describe the synthesis and properties of this substance.

For the preparation of 2-methyl-3,5-diphenylpentene-4-diol-2,3 we employed the method of catalytic hydrogenation of the corresponding acetylenic α-glycol – dimethylphenyl-phenylethinyl-ethylene glycol (2-methyl-3,5-diphenylpentyne-4-diol-2,3) (II) [1]. Pinacones of this type, as shown by E. D. Venus-Danilova and co-workers [2-8], can be readily synthesized by the Zh. I. Iotsich method.

Following the addition of 2 atoms of hydrogen in presence of colloidal platinum, 2 geometrical isomers were isolated: the cis-isomer with m.p. 56-57° and the trans-isomer with m.p. 86-87°. Further hydrogenation of both isomers with platinum black gives one and the same saturated glycol, although the cis-isomer adds on hydrogen twice as quickly as the trans isomer.

The same saturated glycol – 2-methyl-3,5-diphenylpentane diol-2,3 (IV) – was obtained by reduction of the original acetylenic glycol in presence of platinum black.



(II) (III) (IV)

EXPERIMENTAL

Synthesis of 2-Methyl-3,5-diphenylpentene-4-diol-2,3

The α-glycol was synthesized by the method of catalytic hydrogenation of the acetylenic glycol in the presence of colloidal palladium. The colloidal palladium was prepared on gum arabic by Loew's method [9].

Hydrogenation was carried out in an ordinary hydrogenation flask with mechanical shaking. Hydrogen was charged into the reaction flask in quantity necessary for conversion of the triple bond into a double bond. One of the experiments is detailed in Table 1.

From the data of Table 1 we see that hydrogen absorption proceeds smoothly. After separating the catalyst and dissolving off the solvent, colorless crystals were obtained which were washed on the filter with cold ligroin.

The ligroin insoluble substance melted at 86-87°. After driving off the ligroin and repeated crystallizations,

TABLE 1

2.66 moles acetylenic glycol; 50 ml alcohol; 5 mg Pd (6 ml Pd). Pressure 759 mm, temp. 20°, calculated H_2 242 ml

T.....	5	10	15	20	25	30	35	40	45
v.....	38	78	110	133	156	178	200	222	242
% H_2....	15.7	32.2	54.4	54.9	64.4	73.1	82.6	91.7	100

T is the time in minutes from the start of the experiment; v is the volume of hydrogen absorbed from the start of the experiment; % H_2 is the volume of hydrogen in percentages.

a substance with m.p. 56-57° was isolated from the mother liquor. The melting points of both substances did not change after recrystallization from hot ligroine. Both substances decolorize bromine water and aqueous potassium permanganate. The molecular data show that the two compounds have the same composition and molecular weight. Hydrogenation of both substances in presence of platinum black gives one and the same saturated glycol with m.p. 72-73°.

On the basis of these data we may conclude that the crystals with m.p. 56-57° and 86-87° are geometrical isomers and that, apparently, the one with m.p. 56-57° is the cis-isomer and the other the trans-isomer.

Examination of the Trans-Isomer with m.p. 56-57°.

0.0758 g substance: 0.2212 g CO_2; 0.0500 g H_2O. Found %: C 81.10; H 7.38. $C_{18}H_{26}O_2$. Calculated %: C 80.60; H 7.83.

0.0934 g substance; 11.00 g C_6H_6: Δt 0.16°. Found: M 265.9. $C_{18}H_{26}O_2$. Calculated: M 268.

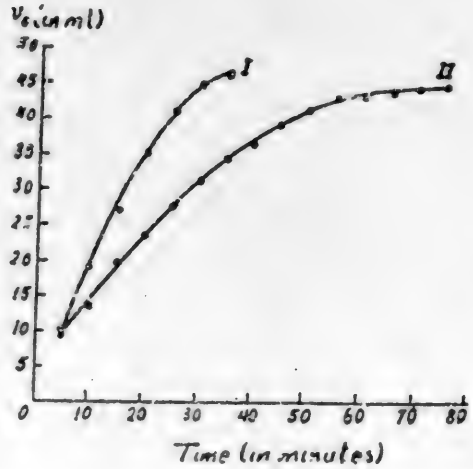
0.0232 g substance: 4.4 ml CH_4 (15°, 757 mm). Found: v_0 4.0 ml; % OH 13.23. $C_{18}H_{18}(OH)_2$. Calculated: v_0 3.86 ml. % OH 12.75.

The compound is readily soluble in common solvents: with strong sulfuric acid it gives a bright-red coloration with a marked greenish fluorescence which disappears on dilution with water.

Addition of two atoms of hydrogen to the cis-isomer proceeds fairly quickly, as is evident from the diagram (curve I—cis-isomer).

Hydrogenation was carried out with 0.5 g glycol. 0.3 g platinum black and 25 ml alcohol; pressure 758 mm, temp. 16°. Theoretical amount of hydrogen 45 ml.

After separating the catalyst and distilling off the solvent, colorless crystals with m.p. 72-73° were obtained which did not decolorize bromine water and potassium permanganate.



Examination of the Trans-Isomer, m.p. 86-87°

0.0524 g substance: 0.1571 g CO_2; 0.0412 g H_2O. Found %: C 81.75; H 8.89. $C_{18}H_{20}O_2$. Calculated %: C 80.60; H 7.83.

0.0950 g substance: 11.02 g C_6H_6: Δt 0.16°. Found: M 269.6. $C_{18}H_{26}O_2$. Calculated: M 268

0.048 g substance: 8.5 ml CH_4 (15°, 757 mm). Found: v_0 8.2 ml; % OH 13.00 $C_{18}H_{18}(OH)_2$. Calculated: v_0 8.0 ml; % OH 12.69.

The substance is sparingly soluble in cold ligroin: it dissolves in ordinary organic solvents. With strong sulfuric acid it slowly gives a dark-red coloration which persists for a long period. On dilution with water the color disappears.

Addition of two atoms of hydrogen led to isolation of crystals with m.p. 72-73°, which did not give a melting point depression with the substance obtained by hydrogenation of the cis-isomer. The trans-isomer adds on hydrogen twice as slowly as the cis-isomer, as shown in the diagram (curve II—trans-isomer).

The quantities of reagents and the conditions for hydrogenation of the trans-isomer were similar to those for the cis-isomer.

Preparation of 2-Methyl-3,5-diphenyl-pentanediol-2,3

The saturated glycol was prepared by hydrogenation of the acetylenic glycol both in presence of colloidal palladium and in presence of platinum black. Results are set forth in Tables 2 and 3.

Hydrogen adds on smoothly to the acetylenic glycol to form the saturated glycol; no halt in the velocity of hydrogenation was observed after addition of 2 atoms of hydrogen, such as had been observed for γ-acetylenic glycols [10]; a crystalline substance with m.p. 72-73° was isolated in both cases after addition of 4 atoms of hydrogen.

TABLE 2

2.56 g (0.01 mole) acetylenic pinacone; 50 ml ethyl alcohol; 6 mg Pd (6 ml Pd). Pressure 755 mm, temp. 20°, calculated $2H_2$, 488.2 ml

T. . .	3	6	9	12	15	18	21	24	27	30	33	35	40
ν. . .	108	192	256	309	352	386	413	437	457	473	481	487	490

TABLE 3

1.33 g (0.0051 mole) acetylenic glycol; 50 ml alcohol; 0.4 g platinum black. Pressure 779.5 mm, temp. 16°, calculated $2H_2$, 234 ml

T. . .	10	20	30	40	50	60	70	80	90	100	110	120	130
ν. . .	50	85	113	137	159	177	193	207	217	224	228	232	234

Investigation of the Saturated Glycol with m.p. 72-73°.

0.1029 g substance: 0.3025 g CO_2; 0.0760 g H_2O. Found %: C 80.40; H 8.30; $C_{18}H_{22}O_2$. Calculated %: C 80.00; H 8.10.

0.2096 g substance; 12.36 g C_6H_6; Δt 0.31°. Found: M 273.5. Calculated: M 270.0.

0.0252 g substance: 4.5 ml CH_4 (15°, 755.5 mm). Found: ν_0 4.2 ml %OH 12.68. $C_{18}H_{20}(OH)_2$. Calculated ν_0 1.18 ml; % OH 12.58.

The glycol with m.p. 72-73° (from ligroin) did not decolorize bromine water and aqueous potassium permanganate; in presence of strong sulfuric acid it carbonizes; it dissolves in the common organic solvents.

Oxidation of the saturated glycol with manganese triacetate [11]. To a flask containing 6.5 g manganese triacetate and 100 ml glacial acetic acid was added a solution of 5 g of the saturated glycol (m.p. 72-73°) in 100 ml glacial acetic acid over a period of 5 hours at 80-85° with constant stirring. After completion of the reaction, the solution had acquired a lemon-yellow color. On cooling, a precipitate of manganese diacetate came down and was filtered off. The filtrate was neutralized and distilled with steam; the distillate was extracted with ether; acetone was detected in the aqueous residue from the distillate; after salting-out, it was distilled into a solution of 2,4-dinitrophenylhydrazine. The resultant acetone 2,4-dinitrophenylhydrazone had m.p. 125-126° and did not give a melting point depression with authentic acetone 2,4-dinitrophenylhydrazone.

From the ethereal extract was isolated 0.7 g of the crystalline substance with m.p. 71-72°. Its oxime had m.p. 82-83°. These melting points correspond to those of 1,3 diphenylpropanone-1, which has been described in the literature [12]. The dinitrophenylhydrazone of this ketone (yellow needles) had m.p. 142-144°.

SUMMARY

1. 2-Methyl-3,5-diphenylpentene-4-diol-2,3 was synthesized by catalytic hydrogenation of 2-methyl-3,5-diphenylpentyne-4-diol-2,3 in presence of colloidal palladium.

2. Two geometrical isomers of the olefinic glycol were isolated and characterized: m.p. 56-57° and 86-87° (cis- and trans-isomers).

3. It was shown that a saturated glycol with m.p. 72-73° is obtained by reduction of the cis- and trans-isomers of the olefinic glycol with platinum black as well as by reduction of the acetylenic glycol both with platinum black and colloidal palladium.

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* See Consultants Bureau Translation, p. 87.
** " " " " " 2477.
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SYNTHESIS AND TRANSFORMATIONS OF ACETYLENIC ALCOHOLS CONTAINING POLYMETHYLENE RINGS

I. 1-PHENYLETHINYL-CYCLOPENTANOL-1

E. D. Venus-Danilova and M. V. Gorelik

Hydration of tertiary acetylenic alcohols of the type of $RR_1C(OH)-C\equiv CH$ usually leads to tertiary α-keto-alcohols with an acetyl group: $RR_1C(OH)-COCH_3$ [1].

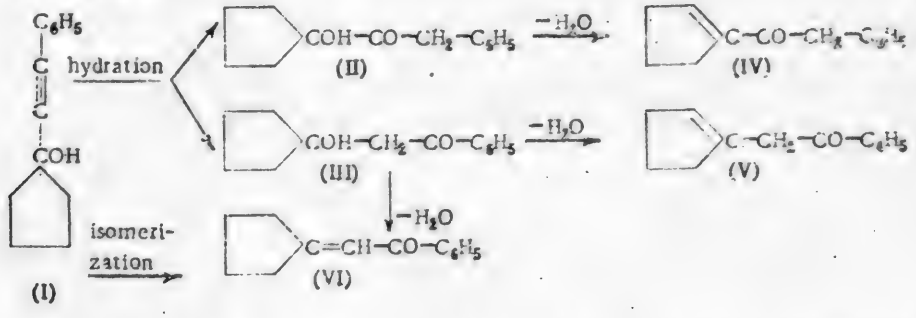
Hydration of tertiary alcohols containing a vinylacetylenic residue has been studied by I.N. Nazarov and co-workers [2, 3]. In this case, in presence of mercuric sulfate and sulfuric acid, the alcohols isomerize to form substituted divinyl ketones and products of their further transformation – substituted tetrahydrofurans.

We have investigated the hydration of tertiary alcohols containing substituted acetylenic residues as well as polymethylene rings by the method of M.G. Kucherov under Scheibler's conditions [4].

As the first object for investigation we selected 1-phenylethinyl-cyclopentanol-1 (I), an interesting compound in that, according to the data of I.N. Nazarov, such a tertiary vinylacetylenic alcohol with a pentamethylene ring forms a divinyl ketone in very low yield by treatment with mercuric sulfate in mild conditions in acetone solution, whereas at a higher temperature the alcohol is dehydrated with considerable resinification [3].

1-Phenylethinyl-cyclopentanol-1 (I), not previously known, was synthesized by Zh. L. Iotsich's method. The structure of the alcohol was established by analyses and from the composition of the products of its oxidation (benzoic and hydroxycyclopentane carboxylic acids).

On hydration of the acetylenic alcohol (I) the formation is possible of α (II) and β (III) ketoalcohols, while their dehydration could lead to the unsaturated ketones (IV), (V) and (VI); in the event, however, of isomerization of 1-phenylethinyl-cyclopentanol-1 (I), another possibility is formation of an unsaturated ketone (VI) – cyclopentylidene-acetophenone.



Investigation of the products obtained by the action of mercuric sulfate and sulfuric acid on 1-phenylethinyl-cyclopentanol-1 (I) showed that the sole product of this reaction is the unsaturated ketone, cyclopentylidene-acetophenone (VI), whose structure was established by oxidation with potassium permanganate (cylcopentanone, glutaric acid and benzoic acid were isolated), by ozonolysis (cyclopentanone and benzoic acid were isolated) and by the preparation of the corresponding pyrazoline.

α-Δ'-Cyclopentenyl-acetophenone (V) has been described in the literature [5]; the constants and properties of this ketone do not agree with those of the unsaturated ketone that we prepared. It has also been reported that condensation of cyclopentanone with acetophenone does not give an olefinic ketone (neither V nor VI). Formation

of cyclopentylidene-acetophenone (VI) could result from hydration of the original acetylenic alcohol to a β-ketoalcohol (III) with further dehydration of the latter; another possibility is the direct isomerization of 1-phenylethinyl-cyclopentanol.

The β-ketoalcohol (III) is bound to possess very labile hydrogen atoms in the methylene group and is easily dehydrated with formation of cyclopentylideneacetophenone; consequently, it cannot be detected in the reaction products.

The second hypothesis is also probable, bearing in mind the increased lability of the hydroxyl group standing in the α-position to the triple bond, as confirmed by the numerous investigations of many chemists [6]. This lability of the hydroxyl group and the susceptibility of the acetylenic alcohol to the acetylene-allene rearrangement is intensified by the presence of the phenyl group and by the acid catalyst.

Experiments with use of a more dilute solution of mercuric sulfate and a lower content of free sulfuric acid, also experiments with sulfuric acid alone, enable clarification of the course of the transformation of 1-phenylethinyl-cyclopentanol-1 into cyclopentylidene-acetophenone.

EXPERIMENTAL

1-Phenylethinyl-cyclopentanol-1 (I)

Synthesis. We describe one of the experiments on preparation of 1-phenylethinyl-cyclopentanol-1 starting from 12 g magnesium, 64 g ethyl bromide, 51 g phenylacetylene and 42 g cyclopentanone. Preparation of the phenylethinylmagnesium bromide proceeded normally with evolution of the theoretical amount of ethane. The ethereal solution of cyclopentanone was run in slowly, with stirring and cooling to 0°. The obtained complex was decomposed carefully with 8% sulfuric acid; the ether extract was washed with dilute aqueous sodium carbonate solution and dried with sodium sulfate. The ether was driven off to leave a viscous, dark liquid (90 g) which did not crystallize on standing. The residue of unreacted phenylacetylene was distilled off in vacuum (b.p. 49-51° at 25 mm); after this, however, the substance did not crystallize and set to a yellow-brown mass. At 1 mm pressure the substance boiled at 113-118° with partial decomposition, forming a semisolid mass which did not give definite crystals.

The residue after removal of the phenylacetylene was purified by dissolving it in a small amount of ethyl alcohol (or methyl alcohol) and diluting the solution with 20-25 times the amount of cold water. An emulsion was formed which, after a day, deposited long, slender crystals resembling glass wool. In the dry condition they resembled felt and had m.p. 41-42°. In this method of purification, all the resinous impurities either floated to the surface to form a solid film or sank to the bottom. By repeated solution and precipitation with water of the impurities it was possible to isolate an additional considerable amount of the pure substance. The procedure results in considerable losses of material (yield 30-35% of the theoretical), but the product is obtained in a very pure form, especially if dissolution and reprecipitation are performed twice.

0.1505 g substance: 0.4509 g CO_2; 0.1054 g H_2O. 0.1114 g substance. 0.3416 g CO_2; 0.0762 g H_2O. 0.1866 g substance; 12.54 g C_6H_{12}; Δt 0.30°. 0.0763 g substance. 11.7 ml CH_4 (20°, 769 mm). 0.0606 g substance: 9.0 ml CH_4 (29°, 768 mm). Found %: C 83.28, 83.61; H 7.78, 7.60. M 190. No. hydroxyl groups 1.17. $C_{13}H_{14}O$. Calculated %: C 83.87; H 7.53. M 186. No. of hydroxyl groups 1.

Oxidation. 5 g acetylenic alcohol was oxidized with 8.4 g potassium permanganate; 400 ml of 1% permanganate solution was run into the alcohol with stirring, and the remaining 4 g of oxidizing agent was introduced in the dry, finely pulverized form with progressive decolorization of the solution.

At the end of the oxidation, the reaction mass was heated to 50-55° and the manganese dioxide was filtered off; an ether extraction was performed to remove neutral products. After the ether had been distilled off, no neutral products were found. The salts of the organic acids were inspissated and decomposed with dilute sulfuric acid, and the precipitated solid acids (3.5 g) were filtered off. M.p. 113°. A portion of these acids was converted into the silver salts by heating with freshly precipitated silver carbonate; the silver contents were determined in the silver salts after fractional recrystallization.

First fraction 0.0803 g salt: 0.0378 g Ag; % Ag 47.07; 0.1111 g salt: 0.0472 g Ag; % Ag 47.15. Fraction 4 0.0913 g salt: 0.0418 g Ag; % Ag 45.78; 0.1082 g salt. 0.0495 g Ag; % Ag 45.84. $C_7H_5O_2Ag$. Calculated %: Ag 47.16. $C_6H_9O_2Ag$. Calculated %: Ag 45.57.

Analysis of the silver salts shows that oxidation gave a mixture of benzoic and hydroxycyclopentane carboxylic acids.

Pure benzoic acid with m.p. 120-121° was isolated from the mixture by sublimation and its structure was confirmed by a mixed melting test with an authentic specimen.

After the solid acids had been removed, ether extraction of the solution yielded a light-yellow, viscous substance which crystallized on standing. After purification, it melted at 102-103°. The acid was converted into a silver salt whose analysis corresponded to the silver salt of α-hydroxycyclopentane carboxylic acid.

0.1100 g substance: 0.1211 g CO_2; 0.0442 g H_2O; 0.0504 g Ag. Found %: C 30.02; H 4.46; Ag 45.82. $C_6H_9O_3Ag$. Calculated %: C 30.38; H 4.22; Ag 45.57.

Transformation of 1-Phenylethinyl-cyclopentanol-1

16 g 1-phenylethinyl-cyclopentanol-1 and 60 ml of a solution of mercuric sulfate, in sulfuric acid [prepared from 5 g HgO, 25 ml H_2SO_4 (sp.g. 1.84) and 150 ml H_2O] [7] was heated for 3 hours at 60-70°. Ether extraction was carried out, the extract was washed with dilute sodium carbonate and water, and dried with sodium sulfate. The residue, after removal of the ether, weighed 16.1 g and after two distillations (7 mm) gave the following fractions:

1) b.p. 145-147°; n_D^{18} 1.585 — 1.1 g; 2) b.p. 147-150°; n_D^{18} 1.582 — 2.0 g; 3) b.p. 150-151°; n_D^{18} 1.580 — 5.8 g; 4) b.p. 151-152.5°; n_D^{18} 1.580 — 5.2 g; in the residue after fractionation — 1.1 g resins.

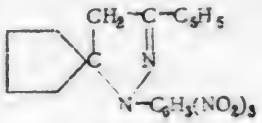
The third and fourth fractions were combined and subjected to investigation.

0.2404 g substance: 0.7312 g CO_2; 0.1666 g H_2O. 0.1201 g substance: 0.3681 g CO_2; 0.0838 g H_2O. 0.2286 g substance; 16.21 g C_6H_6: Δt 0.39°. Found %: C 83.52, 83.59; H 7.70, 7.76. M 184.6. $C_{13}H_{14}O$. Calculated %: C 83.87; H 7.53. M 186.

d_4^{θ} 1.0625; d_{20}^{20} 1.0483; d_4^{20} 1.0465; n_D^{18} 1.580. Found MR_D 58.7. $C_{13}H_{14}O$. Calculated MR_D 56.0.

The substance did not give off a gas when reacted with methylmagnesium iodide; it instantaneously decolorized an aqueous solution of potassium permanganate and a solution of bromine in chloroform. With semicarbazide in aqueous alcoholic solution it slowly forms an uncharacteristic precipitate with an indefinite melting point (193-213°) which could not be readily purified.

With 2,4-dinitrophenylhydrazine, there is at once formed an orange-red, finely crystalline precipitate which, after crystallization from boiling ethyl alcohol melts at 157-158°, gives pyrazoline reactions, and has an analysis corresponding to



0.0873 g substance: 11.7 ml N_2 (15°, 752 mm). 0.0924 g substance: 12.6 ml N_2 (18°, 733 mm). Found %: N 15.2, 15.43. $C_{19}H_{18}O_4N_4$. Calculated %: N 15.33.

Oxidation. To 3 g substance with b.p. 150-152.5° (7 mm) was gradually added 320 ml 1% aqueous solution of potassium permanganate. The reaction is very energetic, decolorization being instantaneous; 2 g of the oxidant was introduced gradually in the dry form. After introduction of the theoretical amount of potassium permanganate (5.2 g), the oxidation was taken still further by addition of a fresh quantity of permanganate. The manganese dioxide was filtered off and washed with a little water. The filtrate was subjected to boiling to drive off volatile, neutral products of oxidation which were collected in semicarbazide solution. A semicarbazone came down immediately; it weighed 0.81 g in the dry state and melted at 204° after recrystallization. A lowering of the melting point was not observed in admixture with an authentic specimen of cyclopentanone semicarbazone. Yield of cyclopentanone (converted from the semicarbazone) 36% of the theoretical.

The salts of the organic acids were concentrated and decomposed with dilute sulfuric acid. A voluminous precipitate came down and was identified as benzoic acid by the usual tests. The filtrate after removal of the benzoic acid, was extracted with ether; the ether was driven off from the extract to leave an acid with m.p. 95-96°, which was converted to the silver salt. The latter was fractionally crystallized. Analysis of the third fraction of silver salts corresponded to the salt of glutaric acid; the first fraction was contaminated with silver benzoate.

First fraction 0.1303 g salt: 0.0758 g Ag; % Ag 58.17. Third fraction 0.1293 g salt: 0.0801 g Ag; % Ag 62.20. $C_5H_6O_4Ag_2$. Calculated %: Ag 62.43. $C_7H_5O_2Ag$. Calculated %: Ag 47.16.

The absence of benzoylformic acid from the oxidation products and the presence of a small quantity of cyclopentanone are evidence that oxidation of the initial products of oxidation – benzoylformic acid and cyclopentanone – continued to benzoic and glutaric acids.

Ozonolysis was performed in chloroform followed by isolation of the neutral and acidic products as in the preceding experiment. Ozonolysis of 3 g substance gave 1.5 g cyclopentanone semicarbazone (not recrystallized), corresponding to 0.91 g cyclopentanone (66 % of the theoretical).

From the acids obtained by acidification of the salts was isolated only 1.4 g unpurified benzoic acid (73.7%). Although the aqueous solution of the acids gave a weak qualitative reaction for benzoylformic acid (yellow flocculent precipitate with aqueous phenylhydrazine hydrochloride [8]), we failed to isolate it in the pure form or in the form of silver salt, due to its negligible amount.

The products of ozonolysis of the unsaturated ketone – cyclopentanone and benzoic acid* (product of decomposition of benzoylformic acid) – confirm the structure of cyclopentylidene-acetophenone.

SUMMARY

1. 1-Phenylethinyl-cyclopentanol-1 was synthesized by Zh. I. Iotsich's method.

2. It was shown that under the conditions of M G. Kucherov's reaction, 1-phenylethinylcyclopentanol-1 is transformed into cyclopentylidene-acetophenone.

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* Evidently the benzoylformic acid decomposed during decomposition and heating of the ozonides.

** See Consultants Bureau Translation, page 159.

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SYNTHESIS AND PROPERTIES OF ETHERS OF DISECONDARY γ-GLYCOLS

III. PREPARATION OF BUTYL AND ISOAMYL ETHERS OF DIPHENYLBUTYNEDIOL, DIPHENYLBUTENEDIOL AND DIPHENYLBUTANEDIOL

Yu. S. Zalkind*, E. D. Venus-Danilova and V. N. Mikhailova

We have previously [1] described the synthesis of the full methyl, ethyl, propyl and isopropyl ethers of diphenylbutynediol, diphenylbutenediol and diphenylbutanediol.

In this paper we describe the preparation of the full butyl (Ia) and isoamyl (Ib) ethers of diphenylbutynediol and their hydrogenation to the corresponding ethers of the olefinic series (IIa and b) and of the saturated series (IIIb) by the procedure described in the previous communication [1].

$$\underset{\text{(Ia and b)}}{C_6H_5-CH(OR)-C\equiv C-CH(OR)-C_6H_5} \xrightarrow[Pd]{H_2} \underset{\text{(IIa and b)}}{C_6H_5-CH(OR)-CH=CH-CH(OR)-C_6H_5} \xrightarrow[Pt]{H_2}$$

$$\longrightarrow \underset{\text{(IIIb)}}{C_6H_5-CH(OR)-CH_2-CH_2-CH(OR)-C_6H_5}$$

Ia R = C_4H_9; Ib R = C_5H_{11} iso; IIa R = C_4H_9; IIb R = C_5H_{11} iso; IIIb R = C_5H_{11} iso.

EXPERIMENTAL

1. Synthesis of Butyl and Isoamyl Ethers of Diphenylbutynediol (Ia and b)

These ethers were synthesized by Mamedov's method [2] from diphenylbutynediol with m.p. 140-142° prepared by Iotsich's method [3].

The results of experiments on the preparation of the butyl and isoamyl ethers of diphenylbutynediol are set forth in Table 1.

TABLE 1

Expt. No.	Amount of diphenylbutynediol (in g)	C_4H_9OH (in ml)	$C_5H_{11}OH$-iso (in ml)	H_2SO_4 (sp. gr. 1.83) (in ml)	Duration of reaction (in hours)	Temp. (in °) of expt.	Temp. (in °) of boiling of the corresponding ether	Yield of ether (in g)	Yield of ether (in %)
1	5	50	–	2	6	80-90	200-207 (3mm)	2.45	16.60
2	5	50	–	2	7	80-90	200-207 (3mm)	2.45	16.60
3	7	50	–	2.5	24	80-90	200-205 (3mm)	5.7	38.77
4	10	50	–	2.5	19	80-90	200 (3mm)	5.1	34.70
5	10	50	–	2.5	21	80-90	200-205 (3mm)	6.5	44.21
6	10	50	–	2.5	24	80-90	200-207 (3mm)	6.0	40.81
7	10	–	50	2.5	24	80-90	210-215 (3mm)	5.4	34.00
8	10	–	50	2.5	17	80-85	205-215 (3mm)	4.8	32.26
9	10	–	50	2.5	24	80-85	210-215 (3mm)	5.0	31.48

The obtained ethers of diphenylbutynediol react with methylmagnesium iodide, which indicates the presence of a mixture of full and partial ethers of diphenylbutynediol. For the purpose of isolating the full ethers of diphenylbutynediol, chemical purification was effected by our previously described method [1]. It must be pointed out, however, that on treating the mixture of ethers of diphenylbutynediol with ethylmagnesium bromide, the formed organomagnesium complex dissolves in the ether ether; the reaction must consequently be carried out in a medium of dry benzene.

*Deceased.

TABLE 2

Properties of Ethers of Diphenylbutyne-, Diphenylbutene- and Diphenylbutanediols

Formula of ether	Boiling point	d_{20}^{20}	n_D^{20}	Mol. wt. found	Mol. wt. cal.	MRD found	MRD calc'd	%C found	%C calc'd.	%H found	%H calc'd
Ia $C_{24}H_{38}O_2$	202-204 (3mm)	1.0018	1.5333	362	350	107.23	107.11	82.10	82.28	8.63	8.57
Ib $C_{28}H_{46}O_2$	212-214 (3mm)	0.9924	1.5269	380.6	378	117.08	116.36	82.34	82.54	9.11	8.99
IIa $C_{24}H_{42}O_2$	175-180 (2mm)	0.9910	1.5253	348.9	352	107.23	107.15	81.75	81.82	9.28	9.09
IIb $C_{28}H_{50}O_2$	180-182 (2mm)	0.9880	1.5300	377.1	380	118.73	117.92	81.95	82.10	9.60	9.47
IIIb $C_{28}H_{54}O_2$	158-158 (3mm)	0.9860	1.5252	378.0	382	118.76	118.39	81.50	81.67	10.10	9.94

The purification led to isolation of the full butyl and isoamyl ethers of diphenylbutynediol.

The properties of the prepared ethers of diphenylbutynediol are set forth in Table 2.

The partial ethers of the glycol in question were not subjected to investigation due to their insignificant amounts.

Hydrolysis of the full butyl ether and the full isoamyl ether of diphenylbutynediol. Hydrolysis was performed with 2 g of the butyl ether of diphenylbutynediol (b.p. 202-204° at 3 mm) and 50 ml 7% sulfuric acid. The reaction was effected by heating to 70-85° with continuous stirring for 10 hours. At the end of the reaction, neutralization was performed with sodium carbonate solution and the reaction products were extracted with ether. After drying and driving off the ether, a nearly colorless liquid was obtained from which crystals came down after a short interval. These melted at 140° after recrystallization from aqueous alcohol and did not give a melting point depression with pure diphenylbutynediol.

Consequently, the formation of diphenylbutynediol on hydrolysis confirms the structure of the original ether.

II. Bromination of the Butyl (Ia) and Isoamyl (Ib) Ethers of Diphenylbutynediol

To a solution of 1 g of the full butyl ether of diphenylbutynediol in 15 ml dry chloroform was added dropwise with continuous stirring 9 ml of a 10% solution of bromine in chloroform (amount calculated for 4 atoms of bromine per molecule of initial ether). After 8 hours' heating at 40° with constant stirring and 12 hours' standing, the reaction mixture retains its dark-yellow color. Evolution of hydrogen bromide during the reaction period was not observed.

The nonreacted bromine was removed by washing with sodium carbonate solution and water. After the reaction mixture had been dried, the ether was driven off, leaving in the distillation flask a fairly viscous liquid (weight 0.85 g) which decomposed when fractionated in vacuum. For this reason the products of bromination were analyzed immediately after removal of the excess of bromine and distillation of the solvent.

0.1824 g substance. 0.1310 g AgBr. 0.1646 g substance. 0.1191 g AgBr. Found %: Br 30.55, 30.78. $C_{24}H_{38}O_4Br_2$. Calculated %: Br 31.35. 0.2047 g substance. 20.20 g C_6H_6. Δt 0.19°. Found: M 515.30. $C_{24}H_{38}O_2Br_2$. Calculated: M 509.83.

The obtained bromide is a fairly viscous, yellow liquid, with good solubility in acetone and chloroform, poor in alcohol. It does not decolorize bromine water and potassium permanganate solution. It gives a reaction for alkoxy groups (Zeisel), but on quantitative analysis the results are 3-5% less than the theoretical amount.

The analytical data for the prepared bromide of the butyl ether of diphenylbutynediol point to the formation of the dibromide of the olefinic series.

Bromination of the full isoamyl ether of diphenylbutynediol was carried out in a manner similar to that for the butyl ether, but using carbon tetrachloride instead of chloroform. The same results were obtained.

We had previously obtained similar results on bromination of the methyl, ethyl, propyl and isopropyl ethers of diphenylbutynediol.

III. Synthesis of Full Butyl and Isoamyl Ethers of Diphenylbutenediol (IIa and b) and Diphenylbutanediol (IIIb).

The esters of diphenylbutenediol were prepared by addition of 2 atoms of hydrogen to a molecule of the acetylenic ether (Ia and Ib) in presence of colloidal palladium; the esters of the saturated series were prepared by addition of 4 atoms of hydrogen in presence of platinum black.

Hydrogenation and isolation of the reaction products were performed by our previously described method [1]. The obtained ethers of the butenediol and the butanediol are light-yellow liquids, readily soluble in organic solvents.

Hydrolysis in an acid medium and the behavior toward bromine and potassium permanganate confirmed the structure of the full ethers of diphenylbutenediol and diphenylbutanediol. The properties of the synthesized ethers are set forth in Table 2.

SUMMARY

1. The following compounds were synthesized and characterized: The full butyl ether of diphenylbutynediol, the full butyl ether of diphenylbutenediol, the full isoamyl ether of diphenylbutynediol, the full isoamyl ether of diphenylbutenediol and the full isoamyl ether of diphenylbutanediol.

2. The action of bromine on the full butyl and isoamyl ethers of diphenylbutynediol was studied. It was shown that bromine adds on at the triple bond in the proportion of 2 atoms per molecule of acetylenic ether to form a bromoether of the olefinic series.

3. It was established that on hydrogenation of the full butyl and isoamyl ethers of diphenylbutynediol with colloidal palladium, the above-mentioned ethers of diphenylbutenediol can be isolated, while on hydrogenation with platinum black the ethers of diphenylbutanediol can be obtained.

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TERTIARY TRIHYDRIC ALCOHOLS OF THE ACETYLENIC SERIES AND THEIR TRANSFORMATIONS

II. SYNTHESIS OF 3,4,7-TRIMETHYL-5-OCTYNE-3,4,7-TRIOL, 2,5-DIMETHYL-5-(1-HYDROXYCYCLOHEXYL)-3-PENTYNE-2,5-DIOL, AND 2,4-DI-(1-HYDROXYCYCLOHEXYL)-3-BUTYNE-2-OL

V. I. Nikitin and S. D. Savranskaya

In an earlier paper [1] one of us described the synthesis of 2,3,6-trimethyl-4-heptyne-2,3,6-triol, the first simplest representative of a class of tertiary trihydric alcohols of the acetylene series.

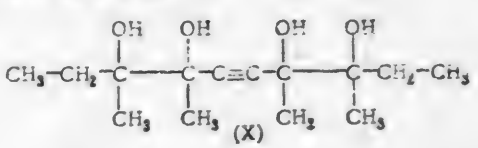
Monohydric alcohols of this series, as well as glycols, have been known for a long time, and many of them have found application not only in the laboratory but also in industrial organic synthesis. A. E. Favorsky and A. S. Onishchenko prepared and described a series of tertiary tetrahydric acetylenic alcohols – erythritols [2, 3]. Of the trihydric alcohols of the acetylenic series, only two primary-secondary alcohols are known:

$HC\equiv C-CHOH-CHOH-CH_2OH$ and $CH_2OH-C\equiv C-CHOH-CH_2OH$,

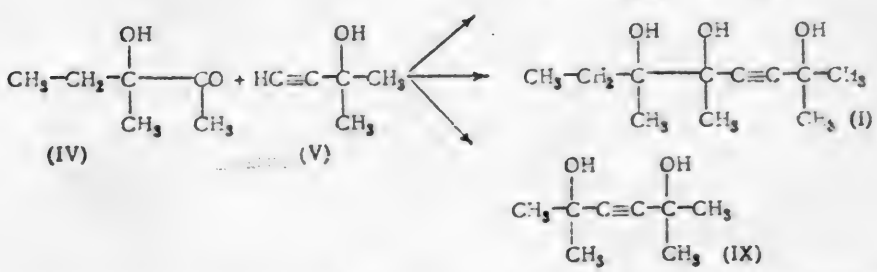
prepared by Lespieau via the organomagnesium synthesis [4, 5]. Respecting tertiary trihydric alcohols of the acetylenic series, these were completey unknown in the literature prior to the above-mentioned synthesis of trimethylheptynetriol.

In the present paper we describe the synthesis of three more trihydric tertiary alcohols of the acetylenic series, starting from acetylenic alcohols and the corresponding hydroxy ketones.

3,4,7-Trimethyl-5-octyne-3,4,7-triol (I) was prepared by condensation of methylethylacetylcarbinol (IV) with dimethylethinylcarbinol (V) according to the scheme:



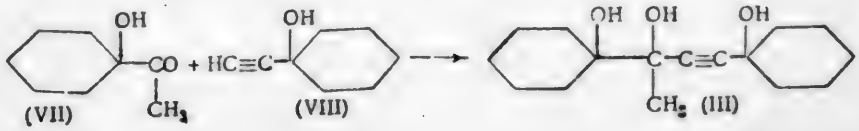
(X)



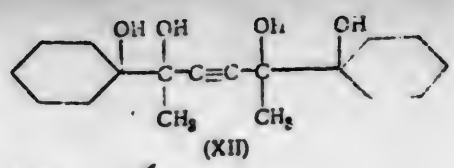
(IV) (V) (I) (IX)

2,5-Dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne-2,5-diol (II) was prepared from acetylcyclohexanol (VI) and dimethylethinylcarbinol (V). (see next page)

2,4-Di-(1-hydroxycyclohexyl)-3-butyne-2-ol (III) was prepared by condensation of acetylcyclohexanol with ethinylcyclohexan-1-ol (VIII).



(VII) (VIII) (III)



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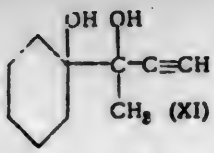

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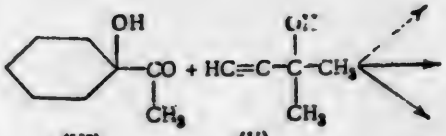

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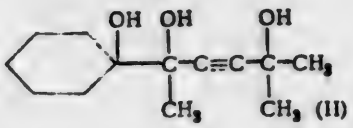

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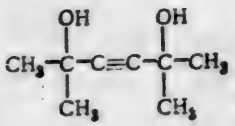

(IX)

A close study of the preparation of these triols revealed the formation of a series of side products as indicated in the above reaction schemes; the detection of these products gives a clearer insight into the mechanism of the reaction.

In the first case, for example, products isolated, apart from 3,4,7-trimethyl-5-octyne-3,4,7-triol (I), were tetramethylbutynediol (IX) and the acetylenic erythritol, 3,4,7,8-tetramethyl-3,4,7,8-tetrahydroxy-5-decyne (X), previously described by A. S. Onishchenko. This author isolated two isomers of this compound with m.p. 111-112° and 155-156°. One of these is a racemate, the other a meso form. We only isolated one isomer with m.p. 155-156°.

In the second case, in addition to the tetrahydric alcohol, 2,5-dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne-2,5-diol, the following were isolated: tetramethylbutynediol (IX), an α-glycol, 2-(1-hydroxycyclohexyl)-3-butyne-2-ol (XI), and a bicyclic erythritol, 2,5-di-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol (XII), the latter not previously described in the literature. The erythritol contains two asymmetric atoms of carbon; we isolated two isomers with m.p. 161-162° and 147-149° (meso form and racemate).

In the third case no side products of reaction could be isolated.

A. I. Zakharova [6] synthesized nonsymmetrical acetylenic γ-glycols by the action of ketones on acetylenic carbinols in the conditions of the Faworsky reaction and obtained — apart from the expected glycol — two more symmetrically constructed acetylenic γ-glycols. These glycols, as Zakharova showed, are formed from the acetylene and the ketone — products of breakdown of the acetylenic alcohols.

Formation of secondary products in our conditions may be explained by a similar breakdown of the acetylenic alcohol introduced into the reaction, i.e., breakdown of dimethylethinylcarbinol into acetylene and acetone. The free acetylene then reacts with two molecules of the ketoalcohol present in the reaction mass and forms an erythritol, in full accord with the data of A. E. Favorsky and A. S. Onishchenko.

Tetramethylbutynediol could have been formed by interaction of acetylene with two molecules of acetone, or by interaction of acetone with dimethylethinylcarbinol.

Concerning the α-glycol, 2-(1-hydroxycyclohexyl)-3-butyne-2-ol (XI), this is evidently formed during distillation in vacuum due to decomposition of 2,5-di-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol (XII) into ketoalcohol and α-glycol. This decomposition is similar to that described by A. E. Favorsky and A. S. Onishchenko for other erythritols.

A. I. Zakharova showed in the above-cited investigation that acetylenic glycols do not appear to undergo decomposition, or only decompose to an insignificant extent.

Trihydric alcohols behave like glycols. We confirmed this by a special experiment. All the acetylenic triols that we obtained were, after 6 hours' stirring with KOH in a medium of dry ether at a temperature of −2 to −3° followed by standing for 12 hours at room temperature, almost completely recovered without any change whatever. In the same conditions monohydric alcohols are partly broken down to ketone and acetylene, from which are immediately formed the corresponding γ-glycols. The stability of the triols is demonstrated indirectly by the fact that the synthesis of 2,4-di-(1-hydroxycyclohexyl)-3-butyne-2-ol (III) was not accompanied by any secondary products; (III), like all monohydric alcohols of the acetylenic series, is a stable compound; the

speed of its formation from acetylcyclohexanol and 1-ethinylcyclohexanol is so high that the acetylene and the cyclohexanol are able to react completely before any side reactions occur, thus giving the trihydric alcohol in high yield. Trihydric alcohols of the acetylenic series are only susceptible to breakdown under the action of alkaline reagents.

The structure of the so-obtained glycerols (I), (II), and (III), which are the main products of reaction, and the structure of the secondary products—the erythritols (X) and (XII) and the glycol (XI)—were verified by heating in presence of potassium carbonate when all the substances in question exhibited the characteristic property of tertiary acetylenic alcohols of breaking down into their original components. In all cases the corresponding hydroxyketones and acetylene were obtained.

EXPERIMENTAL

I. Synthesis of 3,4,7-Trimethyl-5-octyne-3,4,7-triol (I)

Starting materials: dimethylethinylcarbinol and methylethylacetylcarbinol were prepared by the usual methods.

The first was prepared by Favorsky's method: action of acetylene on acetone in presence of KOH in a medium of dry ether.

B.p. 99-101° at 695 mm; d_4^{20} 0.8614; n_D^{20} 1.4204. Found MR_D 24.70; C_5H_8O. Calculated: MR_D 24.81.

The second was prepared by hydration of methylethylethinylcarbinol (Kucherov's method).

B.p. 148-149°; d_4^{20} 0.9402; n_D^{20} 1.4220. Found: MR_D 31.36. Calculated: MR_D 31.45.

A mixture of 23 g dimethylethinylcarbinol and 29 g methylethylacetylcarbinol in 75 ml absolute ether was run dropwise over a period of 3 hours into a flask fitted with a mechanical stirrer and containing 60 g chemically pure powdered KOH and 300 ml absolute ether. The flask was immersed in an ice bath at a temperature of −2 to −3°, which was maintained throughout the whole reaction period. With progressive addition of the mixture to the reaction flask, its contents thickened and became light-yellow. After the reaction mixture had been added, stirring was continued for a short period, after which the mass was left overnight. In the morning the formed complex had settled out as a light-yellow gelatinous mass which was decomposed with 30 ml water while stirring. The ethereal layer was then separated from the aqueous-alkaline layer; the latter was extracted several times with ether and the extracts combined into a single ethereal solution. This ether extract was saturated with carbon dioxide for 4 hours. After drying with sodium sulfate, the ethereal layer was filtered off and the ether distilled off. Weight of crude product 50 g. Fractionation of the latter in vacuum at 3 mm gave the following fractions: 1) 80-128°, 4.25 g, which crystallized; 2) 128-132°, 37.2 g, a viscous liquid; 3) 132-140°, 3.2 g crystals.

The first fraction with b.p. 80-128° at 3 mm consisted almost entirely of tetramethylbutynediol. After recrystallization from benzene it melted at 95-96°. The melting point was not depressed in admixture with an authentic specimen of tetramethylbutynediol.

The second fraction with b.p. 128-132° at 3 mm distilled over almost completely at 118-119° at 2 mm and proved to be 3,4,7-trimethyl-5-octyne-3,4,7-triol, the yield being 71.5 % based on the ketoalcohol taken in the reaction.

d_4^{20} 1.0239; n_D^{20} 1.4796. Found: MR_D 55.45. $C_{11}H_{20}O_3$. Calculated MR_D 55.57.

3.260 mg substance: 7.849 mg CO_2; 3.002 mg H_2O. 8.334 mg substance. 20.096 mg CO_2; 7.720 mg H_2O. Found %: C 65.70, 65.80; H 10.37, 10.36. $C_{11}H_{20}O_3$. Calculated %: C 66.6, H 10. 0.0967 g substance: 37.8 ml CH_4 (19°, 692.1 mm). 0.0911 g substance. 36.2 ml CH_4 (20°, 692.1 mm). Found %: OH 25.30, 25.64. $C_{11}H_{20}O_3$. Calculated %: OH 25.51.

Cleavage of the triol (I) with potassium carbonate. 5.5 g substance was heated in a Wurtz flask in presence of 0.3 g potassium carbonate. Evolution of gas was observed and the gas was led through a side tube into ammoniacal silver oxide solution. When the gas was passed through an ammoniacal solution of cuprous chloride, the characteristic red color of copper acetylide was formed. The precipitate of silver acetylide was filtered off, dried and detonated by a blow. Three fractions were distilled: 1) 80-110°, 0.6 g; 2) 110-145°, 3.0 g; 3) 145-148°, 1.6 g.

In the first fraction were identified acetone (formation of a 2,4-dinitrophenylhydrazone with m.p. 124-125° which did not depress the m.p. of an authentic specimen of acetone phenylhydrazone) and dimethylethinylcarbinol (identified by the Kucherov hydration reaction which proceeded characteristically with intermediate formation of a white, curd-like precipitate which later went into solution with separation of metallic mercury).

In regard to the second and third fractions of decomposition products, boiling at 110-145° and 145-148°, these consisted of methylethylacetylcarbinol; the first of these, however, was contaminated with dimethylethinylcarbinol. Both of these fractions readily formed a semicarbazone (m.p. 150-151°) with semicarbazide hydrochloride and amixed test with authentic methylethylacetylcarbinol semicarbazone did not give a depression of melting point With 2,4-dinitrophenylhydrazine both fractions gave fine, yellow crystals melting (from ethyl alcohol) at 107-108° and not showing a depression in admixture with authentic methylethylacetylcarbinol phenylhydrazone.

The third fraction with b.p. 132-140° was recrystallized from a mixture of equal parts of benzene and ethyl alcohol. The crystals melted at 155-156° and corresponded to the erythritol, 3,4,7,8-tetramethyl-3,4,7,8-tetrahydroxy-5-decyne (X), first described by A. S. Onishchenko.

5.055 mg substance: 11.974 mg CO_2; 4.536 mg H_2O. 5.190 mg substance: 12.274 mg CO_2; 4.688 mg H_2O. Found %: C 64.62, 64.53; H 10.04, 10.11. $C_{14}H_{26}O_4$. Calculated %: C 65.11; H 10.08.

The prepared erythritol did not give a melting point depression with the authentic erythritol synthesized by the method of A. E. Favorsky and A. S. Onishchenko [2, 3] from methylethylethinylcarbinol and acetylene.

Decomposition of the erythritol (X) with m.p. 155-156° by heating with potassium carbonate. 2 g substance and a little potassium carbonate were heated in a small Wurtz flask. At the start of boiling a gas came off which, with ammoniacal silver oxide, gave a white precipitate of silver acetylide. The precipitate was filtered, dried, and detonated by impact. Into the receiver distilled a fraction with b.p. 146-148° (1.2 g) which was identified as methylethylacetylcarbinol (n_D^{20} 1.4209); with semicarbazide hydrochloride it readily forms a semicarbazone with m.p. 150-151° (from methyl alcohol), not giving a depression in admixture with authentic methylethylacetylcarbinol semicarbazide.

II. Synthesis of 2,5-Dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne-2,5-diol (II)

The dimethylethinylcarbinol required for the synthesis was prepared as in the first case and had the same constants. Acetylcyclohexan-1-ol was prepared by hydration of 1-ethinylcyclohexan-1-ol by Kucherov's method and had the following constants: B.p. 52-53° at 3 mm; d_4^{20} 1.0217; n_D^{20} 1.4700. Found: MR_D 38.78. $C_{10}H_{14}O_2$. Calculated MR_D 38.48.

A mixture of 55 g acetylcyclohexanol and 32.5 g dimethylethinylcarbinol in 120 ml dry ether was run dropwise over a period of 4 hours into a flask containing 110 g chemically pure, pulverized KOH in 600 ml dry ether. The reaction conditions were the same as in the preceding synthesis. The solidified mass of reaction products was decomposed with water, during which process a small proportion failed to dissolve. The insoluble residue was filtered off. The ether layer was separated from the aqueous-alkaline layer; the latter was extracted 2-3 times with ether and the ethereal extract was combined with the original ethereal solution.

The precipitate which had not gone into solution in the ether gave, after several recrystallizations from methyl alcohol, colorless crystals with m.p. 161-162° (14.7 g), identifiable as the erythritol, 2,5-di-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol (XII).

0.1643 g substance: 0.4198 g CO_2; 0.1456 g H_2O. 0.1289 g substance: 0.3295 g CO_2; 0.1135 g H_2O. Found %: C 69.52, 69.60; H 9.92, 9.90. $C_{18}H_{30}O_4$. Calculated %: C 69.67; H 9.68.

The structure of the substance was verified by cleavage during distillation in vacuum and over potassium carbonate. Its synthesis was also accomplished.

a) Cleavage of substance with m.p. 161-162° by vacuum distillation. 3 g substance was distilled in vacuum at 21-22 mm. A 2.3 g fraction boiling at 96-100° was collected. A second distillation of this at 20 mm gave 1.4 g with b.p. 99° which was identified as acetylcyclohexanol (n_D^{20} 1.4688). It forms a semicarbazone in the form of white needles, m.p. (from methyl alcohol) 194-195°, and did not give a depression of melting point with the semicarbazone of authentic 1-acetylcyclohexan-1-ol.

b) Cleavage of substance with m.p. 161-162° by heating with potassium carbonate. 2 g of the crystals was heated in a Wurtz flask at normal pressure in presence of a small amount of potassium carbonate; acetylene

was evolved and was converted into silver acetylide by passage into ammoniacal silver oxide. Into a receiver was distilled a liquid fraction with b.p. 196-206° (1.5 g), which was 1-acetylcyclohexan-1-ol. When vacuum-distilled at 7-8 mm, the fraction came over almost completely at 80-82°; (n_D^{20} 1.4683). Its semicarbazone melted at 194-195° and did not depress the melting point of authentic acetylcyclohexanol semicarbazone.

c) Preparation of the erythritol, 2,5-di-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol (XII) by the method of A. E. Favorsky and A. S. Onishchenko. For final proof of the structure of our isolated erythritol as symmetrical dimethyl-di-(1-hydroxycyclohexyl)-butynediol (XII), we prepared it by condensation of acetylcyclohexanol with acetylene.

To 400 ml dry ether and 56 g powdered KOH, through which a stream of acetylene was continuously passed, was added dropwise 30 g acetylcyclohexanol in 200 ml ether. The bath temperature was −5 to −10°. At the conclusion of the reaction, the reaction mass was treated with 50 ml water. The insoluble portion was separated and after recrystallization from ethyl alcohol it consisted of 26.1 g with m.p. 161-162°. A mixed melting test with the crystals that we prepared when synthesizing 2,5-dimethyl-5-(1-hydroxycyclohexyl)-2-pentyne-2,5-diol (II) did not show a depression.

The ethereal solution of the products of synthesis of the erythritol (XII) by the method of Favorsky and Onishchenko was separated from the aqueous-alkaline layer and dried; the ether was distilled off and the products distilled at 3-4 mm. A 2.4 g fraction with b.p. 60-110° was obtained (the residue of 1.5 g in the flask was not examined.)

The fraction with b.p. 60-110° (3mm) crystallized. The crystals melted at 67-68° (from ligroin) and a mixed melting test with the α-glycol 2-(1-hydroxycyclohexyl)-3-butyne-2-ol (XI) isolated in the synthesis of 2,5-dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne)2,5-diol (II) did not give a melting point depression.

From the ethereal solution obtained by extraction of the products of synthesis of 2,5-dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne-2,5-diol (II) was isolated a liquid which after vacuum fractionation (3 mm) gave four fraction: 1) 80-110°, 7.1 g, crystallized; 2) 110-151°, 5.4 g, a liquid; 3) 151-155°, 36.3 g, a viscous liquid which solidified to a transparent vitreous mass; 4) 155-210°, 1.5 g, crystallized.

The first fraction with b.p. 80-110° (3 mm) melted at 95-95° after recrystallization from benzene and corresponded to the tetramethylbutynediol (IX). No depression was found in the melting point determination of the mixture with authentic tetramethylbutynediol.

The second fraction with b.p. 110-151° (3 mm) gave after several redistillations: acetylcyclohexanol (VI) with b.p. 74-78° (5 mm), n_D^{20} 1.4693; semicarbazone with m.p. 193-195° which did not show a depression in admixture with the semicarbazone of authentic acetylcyclohexanol, also 4 g α-glycol 2-(1-hydroxycyclohexyl)-3-butyne-2-ol (XI) with m.p. 67-68°. With ammoniacal silver oxide it forms a characteristic white precipitate indicating the presence of free acetylenic hydrogen.

0.1135 g substance: 0.2980 g CO_2, 0.0981 g H_2O. 0.1359 g substance: 0.3566 g CO_2, 0.1169 g H_2O. Found %: C 71.60, 71.55; H 9.67, 9.63. $C_{16}H_{26}O_2$. Calculated %: C 71.43; H 9.53. 0.0912 g substance: 29.3 ml CH_4 (23°, 700.4 mm). 0.0974 g substance: 30.8 ml CH_4 (22.9°, 699.1 mm). Found %: OH 20.77, 20.42. $C_{16}H_{26}O_2$. Calculated %: OH 20.23.

In the determination of the hydroxyl groups, the first measurement of the gas volume was taken because the gas volume progressively increased on standing, which indicates the presence of free acetylenic hydrogen.

The structure of the acetylenic α-glycol with m.p. 67-68° (XI) was confirmed by decomposition with potassium carbonate when acetylene was identified (precipitate when passed through ammoniacal silver oxide), also 1-acetylcyclohexan-1-ol which was characterized through the semicarbazone with m.p. 193-194°.

The third fraction with b.p. 151-155° (3 mm) was a viscous liquid which solidified on standing till the following day to form a light-green, vitreous mass which was then recrystallized from benzene. White crystals were obtained with m.p. 87-88° which were found to correspond to 2,5-dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne-2,5-diol (II).

4.195 mg substance: 10.633 mg CO_2, 3.700 mg H_2O. 4.640 mg substance: 10.788 mg CO_2, 4.078 mg H_2O. Found %: C 69.17, 69.33; H 9.87, 9.83. $C_{15}H_{26}O_2$. Calculated %: C 69.02; H 9.78. 0.0766 g substance: 26.8 ml CH_4 (19.7°, 686.5 mm). 0.0886 g substance: 31.0 ml CH_4 (22.4°, 692.2 mm). Found %: OH 22.43, 22.41. $C_{15}H_{26}O_2$. Calculated %: OH 22.57.

Behavior toward KOH solution on heating. 5 g substance was heated under a reflux condenser with a solution of 3.5 g KOH in 25 ml water for 4 hours (until gas ceased to come off). With ammoniacal silver oxide the evolved gas forms a white precipitate of silver acetylide, while with ammoniacal cuprous chloride it forms a characteristic red precipitate of copper acetylide. The silver acetylide was filtered off, dried and detonated by a blow. The upper oily layer was extracted with ether, the extract was dried over sodium sulfate, the ether was driven off, and the residual product was distilled in vacuum (3 mm).

The first fraction with b.p. 52-53° weighed 2.9 g; the second fraction with b.p. 53-120° comprised a few drops. The 52-53° fraction, n_D^{20} 1.4690, was acetylcyclohexanol: it readily forms a semicarbazone which melts at 194-195° (from methyl alcohol) and does not give a depression with the semicarbazone of authentic 1-acetylcyclohexan-1-ol.

Consequently the fraction boiling at 151-155° (3 mm), in accord with the data obtained during its investigation, is the trihydric acetylenic alcohol — 2,5-dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne-2,5-diol (II). Its yield, calculated on the acetylcyclohexanol taken in the reaction, is about 43% of the theoretical.

The fourth fraction with b.p. 155-210° at 3 mm was accumulated from several experiments. Recrystallization from benzene enabled two substances to be isolated: one with m.p. 147-149°, the other with m.p. 177-179°. The latter was present in such insignificant amount that it was not amenable to investigation. The compound with m.p. 147-149° corresponded to one of the isomers of 2,5-di-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol (XII).

11.33 mg substance: 29.12 mg CO_2; 10.02 mg H_2O. 12.14 mg substance: 31.30 mg CO_2; 10.73 mg H_2O. Found %: C 70.30, 70.36; H 9.86, 9.88. $C_{18}H_{30}O_4$. Calculated %: C 69.67; H 9.68.
0.0728 g substance: 23.8 ml CH_4 (19.5°, 695.6 mm). 0.0692 g substance: 22.7 ml CH_4 (20.5°, 695.6 mm). Found %: OH 21.19, 21.24. $C_{18}H_{30}O_4$. Calculated %: OH 21.93.

On distillation in vacuum (4-4.5 mm), the substance with m.p. 147-149° broke down into acetylcyclohexanol (semicarbazone with m.p. 194-195°) and 2-(1-hydroxycyclohexyl)-3-butyne-2-ol (XI) with m.p. 67-68°.

Distillation of compound with m.p. 147-149° over potassium carbonate. The gas evolved when 2.6 g of the compound was heated with potassium carbonate was passed through ammoniacal silver oxide and formed silver acetylide. 1.4 g distilled off at 200-206° and formed a semicarbazone with m.p. 194-195° (1-acetylcyclohexan-1-ol).

Consequently its elementary composition, its products of distillation in vacuum and its behavior with potassium carbonate identify the substance with m.p. 147-149° as the erythritol, 2,5-di-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol (XII), which is isomeric with the erythritol with m.p. 161-162°.

III. Synthesis of 2,4- Di-(1-hydroxycyclohexyl)-3-butyne-2-ol (III)

The starting 1-ethinylcyclohexan-1-ol was prepared by the method of A. E. Favorsky and had the following constants:

B.p. 171-172° at 694 mm; m.p. 32-33°; d_4^{25} 0.9734, n_D^{25} 1.4808. Found: MR_D 36.24. $C_8H_{12}O$. Calculated: MR_D 36.42.

Acetylcyclohexanol was prepared as in the preceding synthesis and had the same constants.

A mixture of 53.6 g acetylcyclohexanol and 50 g ethinylcyclohexanol in 150 ml dry ether was run dropwise over a period of 5 hours into a flask containing 110 g chemically pure pulverized KOH and 600 ml dry ether. The reaction conditions and the working-up procedure were similar to those in the preceding syntheses. From the ethereal solution, after driving off the greater part of the ether, white crystals were deposited (89.3 g) which after recrystallization from ligroin melted at 107-108°; yield 86.3% of theory. From the mother liquor after removal of the solvent was recovered 5.6 g ethinyl cyclohexanol with b.p. up to 179° and n_D^{18} 1.4796, and 5.3 g acetylcyclohexanol, n_D^{18} 1.4688 and b.p. 179-205°.

The crystals with m.p. 107-108° were identified as the trihydric alcohol, 2,4-di-(1-hydroxycyclohexyl)-3-butyne-2-ol (III).

0.1894 g substance: 0.5006 g CO_2; 0.1706 g H_2O. 0.2248 g substance: 0.5944 g CO_2; 0.2034 g H_2O. Found %: C 72.07, 72.13; H 10.07, 10.13. $C_{18}H_{30}O_3$. Calculated %: C 72.18; H 9.77.
0.0742 g substance: 22.8 ml CH_4 (22.5°, 694.1 mm). Found %: OH 19.72. $C_{18}H_{30}O_3$. Calculated %: OH 19.17.

Decomposition of compound with m.p. 107-108° by heating with potassium carbonate. 5 g substance and a little potassium carbonate were heated in a Wurtz flask (fitted with a sloping condenser); gas was evolved and formed a white precipitate of silver acetylide with ammoniacal silver oxide and the characteristic red precipitate of copper acetylide with ammoniacal cuprous chloride.

In the receiver was collected 3.9 g liquid products boiling at 170-206°, fractionation of which gave: 0.3 g cyclohexanone (b.p. 154-155°, semicarbazone m.p. 166-167°) and 1-acetylcyclohexan-1-ol (b.p. 99-96° at 6 mm, n_D^{20} 1.4678, semicarbazone with m.p. 194-195°).

Consequently the substance obtained by condensation of 1-ethinylcyclohexan-1-ol with 1-acetylcyclohexan-1-ol corresponds to the tertiary trihydric acetylenic alcohol, 2,4-di-(1-hydroxycyclohexyl)-3-butyne-2-ol (III).

No by-products of this synthesis were isolated.

IV. Behavior of Tertiary Acetylenic Triols in the Conditions of the A.E. Favorsky Reaction

With the aim of establishing the mechanism of formation of the by-products, a study was made of the behavior of the synthesized acetylenic triols in the reaction conditions of their formation.

1) 42 g 3,4,7-trimethyl-5-octyne-3,4,7-triol in 100 ml dry ether was introduced into a flask containing 400 ml dry ether and 60 g chemically pure KOH. The mixture was stirred at a temperature of −2 to −3° for 6 hours and left overnight; the next day it was treated with water. The ethereal layer was separated and the ether was dried and driven off. The residual product was distilled in vacuum (2.5-3 mm) and was identified as the original alcohol; a fraction with b.p. 126-128°, weight 39.2 g, was collected; n_D^{20} 1.4780. Residue in flask 1.9 g. Loss 0.9 g.

2) 19.5 g 2,5-dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne-2,5-diol (II) in 350 ml dry ether and 28 g KOH. Same conditions. 18 g of the substance was recovered unchanged.

3) 5 g 2,4-di-(1-hydroxycyclohexyl)-3-butyne-2-ol (III) in 150 ml dry ether and 10 g KOH. The original alcohol was recovered unchanged (4 g).

We may therefore conclude that trihydric alcohols, like glycols, are stable in the conditions of their synthesis, and that the formation of secondary products must result entirely from partial decomposition of the monohydric acetylenic alcohols described by A. I. Zakharova.

SUMMARY

1. Condensation of tertiary acetylenic alcohols with tertiary acetylcarbinols is a general method for preparation of tertiary trihydric acetylenic alcohols.

2. In addition to trihydric acetylenic alcohols, the reaction yields secondary products in the shape of other tertiary acetylenic alcohols, substituted butynediols, erythritols and α-glycols, due to partial breakdown of the original acetylenic carbinol.

3. The following tertiary trihydric acetylenic alcohols, not previously described in the literature, were prepared: 3,4,7-trimethyl-5-octyne-3,4,7-triol, 2,5-dimethyl-5-(1-hydroxycyclohexyl)-3-pentyne-2,5-diol; and 2,4-di-(1-hydroxycyclohexyl)-3-butyne-2-ol; two isomers of the acetylenic erythritol, 2,5-di-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol, and one new acetylenic α-glycol, 2-(1-hydroxycyclohexyl)-3-butyne-2-ol.

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SYNTHESIS AND TRANSFORMATIONS OF SUBSTITUTED VINYL ETHERS

I. SYNTHESIS OF α-SUBSTITUTED VINYL ETHERS

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Among the unsaturated compounds susceptible to polymerization, special interest is attached to those containing diverse substituents. The effect of the latter is particularly conspicuous not only in respect of the character of the polymerization process but also in respect of the properties of the polymers. It is true that on the basis of our investigations [1] we established that a free-radical and ionic mechanism of polymerization, depending on the reaction conditions, may come into play for one and the same compound. Consequently one or the other form of polymerization is inherent in nearly all vinyl compounds, although observations show that one of them is more easily realized than the other. Ultimately, this depends not only on the structure of the vinyl compounds but also on the polymerization conditions.

Our present investigation is the first in a series devoted to the influence of substituents on the chemical properties and course of the polymerization reactions of substituted vinyl ethers.

Previously we studied [2] the properties and transformations of vinyl ethers (I) which to a certain extent may be regarded as monosubstituted ethylenic derivatives, whereas α-substituted vinyl ethers are the corresponding disubstituted bodies (II)

(I) $CH_2=CH-OR$ (II) $CH_2=\underset{\displaystyle R}{\overset{|}{C}}-OR$.

An α-substituted vinyl ether was prepared for the first time by A. E. Favorsky in 1887 [3] during a study of the mechanism of isomerization of monosubstituted acetylenic hydrocarbons in presence of alcoholic KOH. On acting with alcoholic alkali on allylene, A. E. Favorsky obtained – in place of the anticipated prepadiene — ethylisopropenyl ether (III):

$$CH_3-\underset{\displaystyle OC_2H_5}{\overset{|}{C}}=CH_2 \quad \text{(III)}$$

The same ether (III) was later prepared by Claisen [4] by another method, by heating metals of acetone with phosphorus pentoxide and quinoline.

Moureau [5] considers that the action of alcohol on esters of fatty acids containing a triple bond in presence of the corresponding alcoholates is accompanied by addition of (IV) and that the alcohol (V) is split off on heating. On further heating of (V), these esters undergo hydrolysis with evolution of CO_2 and formation of α-substituted vinyl ethers (VI)

$R-C(OC_2H_5)_2CH_2COOC_2H_5$; (IV)

$R-\underset{\displaystyle OC_2H_5}{\overset{|}{C}}=CH-COOC_2H_5$, (V)

$R-\underset{\displaystyle OC_2H_5}{\overset{|}{C}}=CH_2$ (VI)

Heating of ethynylbenzene with alcohol in presence of concentrated solution of sodium alcoholate leads to formation of the α-substituted vinyl ether (VII), i.e., addition of alcohol takes place in the reverse order to that with compounds of the aliphatic series

$$C_6H_5CH=CH(OCH_3)$$
(VII)

We do not consider this observation to be adequately founded although we shall return to this question in our later communications.

Sherril and Waller [6] obtained α-substituted vinyl ethers in accordance with the scheme:

$$CH_3CHO + C_2H_5OH \xrightarrow[-H_2O]{HCl} CH_3CHCl(OC_2H_5) \xrightarrow[-HCl]{+Br_2} CH_2Br{-}CHBr(OC_2H_5) \xrightarrow{CH_3MgCl}$$

$$\longrightarrow CH_2Br{-}CH(OC_2H_5)CH_3 \xrightarrow[-HBr]{KOH} CH_2{=}C(CH_3){-}OC_2H_5.$$

Hennion, Nieuwland and others [7] showed that on heating the ketal (VIII) with a small quantity of p-toluenesulfonic acid, it readily breaks down with loss of one molecule of alcohol to form the vinyl ether (IX)

$$CH_3{-}C(C_4H_9)(OCH_3)_2 \longrightarrow CH_2{=}C(C_4H_9){-}OCH_3.$$

(VIII) (IX)

In this paper we present the synthesis of α-substituted vinyl ethers, starting from propyne and alcohols in presence of KOH. The synthesis was realized according to the scheme

$$CH_3{-}C{\equiv}CH + ROH \xrightarrow{KOH} CH_2{=}C(R){-}OR$$

TABLE 1

Structure and Constants of α-Substituted Vinyl Ethers

Prep. No.	α-Substituted vinyl ethers	B.p. (°C)	d_4^{20}	n_D^{20}	MR_D Calc.	MR_D Found
1	$CH_3{-}C(OCH_3){=}CH_2$	28 (759 mm)	0.7372	1.3751	21.94	22.30
2	$CH_3{-}C(OC_2H_5){=}CH_2$	63-64 (749 mm)	0.7710	1.3913	26.65	26.92
3	$CH_3{-}C(OC_3H_7){=}CH_2$	78.5 (756 mm)	0.7861	1.3990	31.15	30.87

The reaction of propyne with alcohols proceeds in more drastic conditions than those established by A. E. Favorsky and M. F. Shostakovsky [8] for acetylene. Evidently the change from acetylene, containing two labile hydrogen atoms, to propyne is accompanied by a reduction in the ease of the addition reaction.

The general characteristics of the prepared α-substituted vinyl ethers are set forth in Table 1.

α-Substituted vinyl ethers constitute a class of compounds whose properties have not been closely studied. The conditions of hydrolysis of some members of the class have been studied. A. M. Butlerov [9], A. P. Elnekov [10] and A. E. Favorsky [11] have also studied the course of this reaction and have established the structure of the products of hydrolytic cleavage. The authors showed that hydrolysis of these compounds proceeds according to the scheme

$$CH_3{-}C(OR){=}CH_2 \xrightarrow[H_2SO_4]{KOH} CH_3COCH_3 + ROH.$$

We have utilized this reaction to verify the structure of the prepared α-substituted vinyl ethers.

EXPERIMENTAL

Starting Materials and Procedure for Synthesis

Starting materials were alcohols with the following constants:

1) Methyl alcohol: b.p. 63-64°; d_4^{20} 0.7941, n_D^{20} 1.3304.

2) Ethyl alcohol: b.p. 78.3°; d_4^{20} 0.7892; n_D^{20} 1.3623.

3) Propyl alcohol: b.p. 97.2°; d_4^{20} 0.8044; n_D^{20} 1.3854.

Propyne was selected as the monosubstituted acetylene. It was prepared by bromination of propylene followed by cleavage of two molecules of hydrogen bromide [12].

The so-prepared propyne was dried by passage through a column packed with calcium chloride, and was collected in a previously weighed receiver filled with carbon dioxide and placed in a Dewar flask.

The synthesis was effected in an autoclave. This was cooled to 0 to +2° (snow and salt), and the alcohols used were cooled to −10 to −15°. A definite quantity of propyne weighed into an ampoule was cooled with dry ice and was introduced in the ampoule into the autoclave containing the alcohol and the alkali.

1. Synthesis of α-Methylvinylmethyl ether: $CH_3C(OCH_3)=CH_2$

32 g (1 mole) methanol, 56 g (1.4 mole) propyne and 8.8 g 10% pulverized KOH were charged by the above procedure into a rotating autoclave of the Bergius type (capacity 1 liter), fitted with an electrical heater, a thermometer, and an acetylene gage. The autoclave was hermetically closed and heated for 18 hours at 220-225°. The dependence of the pressure on the temperature is shown in Table 2.

From the data of Table 2 we see that the pressure began to rise appreciably at 160-165°; at 225° it had reached 41 atm. This was followed by a marked fall in pressure in the autoclave. Prior to discharge, the autoclave was cooled (snow + salt). The propyne which had not reacted with the alcohol was collected in a trap placed in a Dewar flask containing carbon dioxide. 6.2 g propyne was collected. The remainder of the reaction mass was transferred from the autoclave to a small flask placed in a freezing mixture (snow + salt).

TABLE 2

Duration	Temp. in autoclave	Pressure in autoclave (in atm.)
0 hrs. 00 min.	20	6
0 hrs 40 min.	105	11.6
1 hr. 20 min.	135	14.6
2 hrs. 30 min.	165	24
3 hrs. 40 min.	200	38
	225	40.5
	225	41
6 hrs. 20 min.	225	39
	225	37.1

Fractionation of the reaction mass, which contained low-boiling products, was performed in a flask with a column on a water bath. The following fractions were collected: 1) b.p. 28° (759 mm), 31.2 g; 2) b.p. 63-64° (759 mm), 12.7 g; resinous residue, 5.7 g.

a) Examination of the fractions. The first fraction of 31.2 g was dried with calcined potassium carbonate and distilled in a column with an efficiency of 20 theoretical plates. A total of 30.2 g came over at 28° (759 mm), leaving traces of the original alcohol in the flask.

Constants of substance with b.p. 28°: n_D^{20} 1.3751; d_4^{20} 0.7372; found M 70.8 (cryoscopically in benzene). C_4H_8O. Calculated M: 72. Found MR_D 22.3. C_4H_8O. Calculated: MR_D 21.94.

Determination of the elementary composition by the combustion method is attended by serious difficulties which detract from the accuracy of the results. We prepared a polymer of the α-substituted vinyl ether and determined its elementary composition.

Found %: C 67.30; H 10.90. C_4H_8O. Calculated %: C 66.90; H 11.00.

The second fraction with b.p. 63-64° is unreacted methyl alcohol with n_D^{20} 1.3307; d_4^{20} 0.7990.

b) Hydrolysis of α-methylvinylmethyl ether. Into a conical flask with a ground glass stopper were introduced 15 g substance and 30 ml 1% H_2SO_4 solution. The reaction mixture was shaken for an hour at room temperature, after which the acid was neutralized with calcined potassium carbonate and the products of hydrolysis were fractionated in a plate column on a water bath. A 56-70° fraction was obtained, comprising a mixture of acetone and methyl alcohol.

Treatment of the mixture with 2,4-dinitrophenylhydrazine gave a precipitate of yellowish-orange crystals which after 2-3 recrystallizations from alcohol had m.p. 127.7°, the same as that of acetone 2,4-dinitrophenylhydrazone. No depression in mixed melting point test (the literature [13] gives m.p. 128°).

The characteristics of the 28° (759 mm) fraction show that reaction of propyne with methyl alcohol in presence of KOH gives α-methylvinylmethyl ether in a yield of about 30% of the theoretical.

2. Synthesis of α-Methylvinylethyl Ether: $CH_3C(OC_2H_5)=CH_2$

The preparation follows the procedure of the previous one.

Into a 1-liter rotating autoclave were charged 56 g (1.4 mole) propyne, 46 g (1 mole) ethyl alcohol, and 10 g KOH. The autoclave was heated for 18 hours at 210-220°. Appreciable rise of pressure set in at 160-170° and reached 37 atm, after which the pressure dropped. The unreacted propyne was collected in a trap (placed in a Dewar flask) after the autoclave had been cooled to room temperature. The Dewar flask was previously filled with carbon dioxide. 19.3 g propyne was collected. The remaining reaction mass was transferred to a small

flask cooled with snow.

Fractionation of the reaction mass, which contained low-boiling products, was performed in a flask with a plate column on a water bath. The following fractions were collected: 1) b.p. 63-64° (749 mm), 46.2 g; 2) b.p. 77-78° (749 mm), 18.6 g; resinous residue, 11.7 g.

a). Examination of the fractions. The first fraction (63-64°) was dried with calcined potassium carbonate and distilled in a column with an efficiency of 20 theoretical plates. A total of 45.5 g came over at 64.1° (751 mm). The compound with b.p. 64.1° had the following constants:

n_D^{20} 1.3913; d_4^{20} 0.7710. Found: M (cryoscopically in benzene) 84.1. MR_D 26.92; Found %: C 69.48; H 11.33. $C_5H_{10}O$. Calculated: M 86; MR_D 26.65; Calculated %: C 69.76; H 11.63.

Literature data [6]: n_D^{20} 1.3913; d_4^{20} 0.7713.

The second fraction with b.p. 77-78° (749 mm) is unreacted ethyl alcohol with n_D^{20} 1.3621; d_4^{20} 0.7890.

b) Hydrolysis of α-methylvinylethyl ether. Hydrolysis was carried out in the above-described conditions. The obtained 2,4-dinitrophenylhydrazone had m.p. 127.4°, the same as that of acetone 2,4-dinitrophenylhydrazone. No depression in mixed test.

The examination of the 64.1° fraction shows that interaction of propyne with ethyl alcohol in presence of KOH leads to α-methylvinylethyl ether in a yield of 30.2% of the theoretical.

3. Synthesis of α-Methylvinylpropyl Ether: $CH_3C(OC_3H_7)=CH_2$.

Into the autoclave were charged 56 g (1.4 mole) propyne, 60 g (1 mole) propyl alcohol, and 10 g KOH. The autoclave was heated for 20 hours at 210-220°. After cooling to room temperature, 13.2 g unreacted propyne was discharged from the autoclave into a trap which was placed in a Dewar flask with carbon dioxide. The remaining reaction mass was transferred to a small flask cooled with snow.

The reaction mass was fractionated in a flask with a plate column (on a bath of Wood's alloy). The following fractions were collected: 1) b.p. 78° (756 mm), 54.2 g; 2) b.p. 97-99° (756 mm), 30.7 g.

a) Examination of the fractions. The 78° fraction was dried with calcined potassium carbonate and fractionated in a column with an efficiency of 20 theoretical plates. The whole of the fraction distilled at 78.5° (756 mm) and had n_D^{20} 1.3990, d_4^{20} 0.7861.

Found: M 102 (cryoscopically in benzene). MR_D 30.77. Found %: C 72.02; H 12.09.
$C_5H_{10}O$. Calculated: M 100. MR_D 31.15. Calculated %: C 72.00; H 12.00.

The 97-99° fraction was unreacted propyl alcohol with n_D^{20} 1.3852; d_4^{20} 0.8041.

b) Hydrolysis of α-methylvinylpropyl ether. The 78.5° (756 mm) fraction was hydrolyzed under the conditions described above. Acetone 2,4-dinitrophenylhydrazone with m.p. 127.0° was obtained. Examination of the 78.5° fraction shows that the reaction of propyne with propyl alcohol in presence of KOH leads to α-methylvinylpropyl ether in a yield of 54% of the theoretical.

SUMMARY

1. The reaction of propyne with methyl, ethyl, and propyl alcohols in presence of pulverized potassium hydroxide leads to formation of α-substituted vinyl ethers: methylvinylmethyl, methylvinylethyl, and methylvinylpropyl ethers.

2. The structure of the α-substituted vinyl ethers was confirmed by their hydrolysis with 1% H_2SO_4 solution. The products of hydrolysis were isolated and characterized.

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FULL AND PARTIAL ESTERS OF β-FURYLACRYLIC ACID AND ETHYLENE GLYCOL

M. E. Egorova and M. A. Abramova

Intensive studies are now in progress in the field of synthesis of esters of acids of the acrylic series with aliphatic alcohols (mono- and polyhydric) as well as with cyclic alcohols.

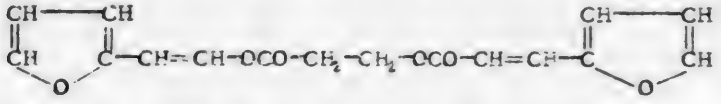
We set ourselves the task of establishing whether esters could be formed from polyhydric alcohols and β-substituted acids of the acrylic series. Esters of β-phenylacrylic acid with ethylene glycol have been prepared and described by us [1].

In the present investigation we established the possibility of formation of esters of ethylene glycol with β-furylacrylic acid. Esters of β-furylacrylic acid with polyhydric alcohols have not been described in the literature, although there are indications [2], that the presence of β-furylacrylic acid in a glycerol ester accelerates the drying of an oil and enhances the quality of the film.

We prepared esters of ethylene glycol with β-furylacrylic acid by the method of direct esterification at the ordinary pressure and a temperature of 150-200°, using an excess of one of the components.

EXPERIMENTAL

I. Preparation of Full Ester of β-Furylacrylic Acid and Ethylene Glycol



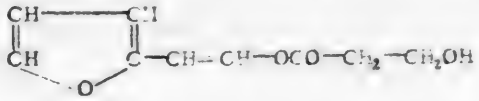
Into a flask, fitted with a gas discharge tube, were introduced ethylene glycol and β-furylacrylic acid (the latter prepared by oxidation of furfurylideneacetone with bleaching powder [3]) in the molar ratio of 1:3 and heated in an oil bath at a temperature of 180-200° for 3 hours. After neutralization with sodium carbonate solution, the residual crystalline product (dirty-yellow color) was separated and washed several times with water (the crystals became lighter in color). After two recrystallizations from alcohol (once in presence of animal charcoal), the product melted at 93-95°.

Found: M 299.1; %: C 63.45, H 4.69 saponification number 355.7. $C_{16}H_{14}O_6$. Calculated: M 302; %: C 63.57; H 4.63, saponification number 370.8.

The analytical data indicate that the crystalline product of reaction of ethylene glycol with β-furylacrylic acid is the full ester.

The product forms light-yellow crystals, readily soluble in acetone, benzene, ether and alcohol (on heating). Yield 48.9% of the theoretical.

II. Preparation of Partial Ester of β-Furylacrylic Acid and Ethylene Glycol



The appropriate amounts of acid and glycol (1:2 molar ratio) were placed in a flask fitted with a gas discharge tube and heated on an oil bath at 160-170° for 4 hours. The reaction product (dark-brown oil) was treated with benzene. The benzene extract was washed with sodium bicarbonate solution and water until neutral and then dried with calcined sodium sulfate. The benzene was distilled off and the residual mass distilled at 28-30 mm. The fraction coming over at 182-184° was analyzed.

Found: M 176.4; n_D^{25} 1.5678; saponification number 304.9, %: C 59.62; H 5.41. $C_9H_{10}O_4$. Calculated: M 182; saponification number 307.6, %: C 59.34; H 5.49.

The yield of purified product is 20-32% of the theoretical. The partial ester is a difficultly mobile, heavy (sp.gr. about 1.3) oil without odor and light-yellow in color; it has good solubility in benzene, alcohol, ether and acetone. In the air the oil quickly turns reddish-brown. When applied to glass in a thin layer, it forms a film (more quickly in the light) which is not lifted by benzene, alcohol or ether.

SUMMARY

The preparation of the full and partial esters of β-furylacrylic acid with ethylene glycol is described.

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** " " " " " 1393.

INTERACTION OF TETRAPHENYLLEAD AND TETRAPHENYLTIN WITH CARBON TETRACHLORIDE IN PRESENCE OF BENZOYL PEROXIDE

Yu. A. Gildekop and R. F. Sokolova

G. A. Razuvaev [1], and later A. E. Borisov [2] showed that in presence of a small quantity of benzoyl peroxide or acetyl peroxide a reaction takes place between carbon tetrachloride and diphenylmercury. The reaction in Borisov's conditions is evidently of the homolytic, radical chain type since it is initiated by stoichiometrically small amounts of peroxides.

We thought it would be interesting to investigate this reaction more closely, and in this paper we have attempted to establish whether the reaction takes place between carbon tetrachloride and phenyl derivatives of other metals. For this purpose we selected tetraphenyllead and tetraphenyltin. These compounds are known to react with carbon tetrachloride under the influence of ultraviolet light [3].

No reactions were observed on prolonged boiling of solutions of tetraphenyllead or tetraphenyltin in carbon tetrachloride in presence of small amounts of a peroxide. Obviously no chain reaction took place. We therefore considerably increased the amount of peroxide; reaction then took place. In these conditions the main reaction product with tetraphenyllead (in presence of benzoyl peroxide) is diphenyllead dichloride; a small amount of diphenyllead dibenzoate is also formed.

Hence the process of dearylation in the case of tetraphenyllead stops at compounds of the type of Ar_2PbX_2.

Other reaction products were chlorobenzene (identified by conversion to 2,4-dinitrochlorobenzene), hexachloroethane, and benzoic and phthalic acids.

On the basis of the above data, we may represent the reaction course by the following scheme:

$$(C_6H_5CO_2)_2 \longrightarrow C_6H_5\cdot + CO_2 + C_6H_5COO\cdot$$

$$CCl_4 + C_6H_5\cdot \longrightarrow C_6H_5Cl + CCl_3\cdot$$

$$(C_6H_5)_4Pb + CCl_3\cdot \longrightarrow (C_6H_5)_3Pb\cdot + C_6H_5CCl_3$$

$$(C_6H_5)_3Pb\cdot + CCl_4 \longrightarrow (C_6H_5)_3PbCl + CCl_3\cdot$$

$$(C_6H_5)_3PbCl + CCl_3\cdot \longrightarrow (C_6H_5)_2PbCl\cdot + C_6H_5CCl_3$$

$$(C_6H_5)_2PbCl\cdot + CCl_4 \longrightarrow (C_6H_5)_2PbCl_2 + CCl_3\cdot$$

$$2CCl_3\cdot \longrightarrow Cl_3C-CCl_3.$$

Benzoic acid may originate from saponification of $C_6H_5CCl_3$.

The presence of diphenyllead dibenzoate among the reaction products may be explained by the following scheme:

$$(C_6H_5)_3Pb\cdot + C_6H_5COO\cdot \longrightarrow (C_6H_5)_3PbOCOC_6H_5$$

$$(C_6H_5)_3PbOCOC_6H_5 + CCl_3\cdot \longrightarrow C_6H_5CCl_3 + (C_6H_5)_2PbOCOC_6H_5$$

$$(C_6H_5)_2PbOCOC_6H_5 + C_6H_5COO\cdot \longrightarrow (C_6H_5)_2Pb(OCOC_6H_5)_2.$$

The reaction between tetraphenyltin and carbon tetrachloride was performed in similar conditions in presence of benzoyl peroxide.

Since the disubstituted tin derivatives of the type of Ar_2SnX_2 are very highly soluble, in this case we get complete dearylation of tetraphenyltin with formation of tin tetrachloride.

Other products of the reaction were chlorobenzene (identified by the usual method), hexachloroethane, and benzoic and phthalic acids. A reaction scheme similar to that proposed above for tetraethyllead could be proposed for the tin compound, except that here the process of dearylation proceeds to completion, to $SnCl_4$.

The only point that still remains obscure is the mechanism of formation of benzoic acid, which could proceed via the phenyl radical, the peroxide or the organometallic compound itself. This problem might be solved by carrying out these reactions in presence of acetyl peroxide.

EXPERIMENTAL

Reaction of Tetraphenyllead with Carbon Tetrachloride in Presence of Benzoyl Peroxide

Into a round-bottomed flask fitted with a condenser (ground-glass joint) was charged a solution of 5.0 g tetraphenyllead in 100 ml carbon tetrachloride. While the reaction mass was boiling, the benzoyl peroxide was introduced in small portions over a period of 8 hours (total amount of peroxide 20 g). After the whole of the peroxide had been added, the reaction mass was boiled for another 50 hours. At the conclusion of the reaction (test with KI for peroxide) the cooled solution was filtered from the precipitate which consisted of $(C_6H_5)_4Pb$ and $(C_6H_5)_2PbCl_2$.

The precipitate was washed with hot toluene which dissolved the tetraphenyllead; after recrystallization from the same solvent it melted at 225°. It did not depress the melting point of authentic tetraphenyllead. Weight 1.7 g, or 34% of the original amount. The toluene-insoluble portion of the precipitate was $(C_6H_5)_2PbCl_2$. Its weight was 2.55 g or 60.8% of the theoretical amount.

Found %: Pb 48.23, 48.12, 48.48. $C_{12}H_{10}PbCl_2$. Calculated %: Pb 47.65.

The filtrate was made alkaline with KOH and distilled with steam. At the termination of the distillation, crystals of hexachloroethane with m.p. 186° (sealed capillary) were extracted from the condenser. There was no melting point depression in admixture with authentic hexachloroethane. Weight 2.43 g.

After removal of water, the distillate was nitrated. A nitro compound was isolated with m.p. 51-52° (from alcohol), weight 1.8 g. There was no melting point depression in a test of this substance with authentic 2,4-dinitrochlorobenzene.

The residue from the steam distillation was filtered and a further small quantity of tetraphenyllead was recovered from it. The main mass of this substance, after recrystallization from alcohol, had m.p. 228-229°. Weight 0.31 g of 5.2% of the theoretical amount. A mixed melting test with the substance prepared specially from tetraphenyllead and benzoic acid likewise gave m.p. 228-229°. This substance was therefore diphenyllead benzoate, as was confirmed by the lead determination.

Found %: Pb 34.34, 34.48. $C_{26}H_{22}O_4Pb$. Calculated %: Pb 34.35.

Addition of hydrochloric acid to the filtrate brought down a white precipitate weighing 2.42 g. This was filtered and dissolved in hot water. The main mass dissolved and had m.p. 120° (from alcohol). A mixture with authentic benzoic acid also had m.p. 120°.

The small quantity of water-insoluble acids contained phthalic acid, as shown by the characteristic fluorescence when fused with resorcinol.

Reaction of Tetraphenyltin with Carbon Tetrachloride in Presence of Benzoyl Peroxide

The reaction of tetraphenyltin with carbon tetrachloride in presence of benzoyl peroxide was effected in conditions substantially similar to those for tetraphenyllead. Reaction components were 5.0 g tetraphenyltin, 10.0 g benzoyl peroxide and 100 ml carbon tetrachloride. At the end of the reaction (50 hours) the precipitate was filtered off and identified as unreacted tetraphenyltin (m.p. 224-225°) which did not give a depression with authentic, pure tetraphenyltin. Weight 0.21 g or 4.2% of the original.

Solvent was removed from the filtrate by distillation on a water bath. The tin chloride formed during the reaction was determined in the form of tin disulfide by precipitation with hydrogen sulfide. The total yield of $SnCl_4$ was 84.1% of the theoretical.

A special experiment was run for the purpose of isolation of the remaining products of reaction (non-organometallic). In this case, alkali was added to the filtrate and steam was passed through. Hexachloroethane with m.p.

108° was isolated. It did not give a depression in a mixed test with authentic material. Weight 2.6 g. The distillate was nitrated and worked up in the usual manner to give a nitro compound with m.p. 51-52°. Weight 1.8 g. This substance did not give a depression of m.p. with pure 2,4-dinitrochlorobenzene. Benzoic acid (2.1 g) and phthalic acid were identified by the same tests as in the previous experiment.

SUMMARY

1. It was shown that interaction of tetraphenyllead with carbon tetrachloride in presence of benzoyl peroxide leads to partial dearylation of tetraphenyltin with formation of compounds of the type of $(C_6H_5)_2PbX_2$, sparingly soluble in organic solvents. Other identified reaction products were chlorobenzene, hexachloroethane and benzoic and phthalic acids.

2. The corresponding reaction of tetraphenyltin with carbon tetrachloride in presence of benzoyl peroxide results in complete dearylation of tetraphenyltin with formation of tin tetrachloride. Other reaction products were chlorobenzene, hexachloroethane, and benzoic and phthalic acids.

3. In conclusion we extend our deep gratitude to G. A. Razuvaev for his constant interest and valuable assistance in the investigation.

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THE SELECTIVE MALONIC SYNTHESIS

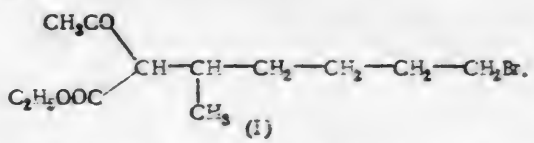
IV. THE ACTION OF SODIO-MALONIC ESTER ON 1,5-DIBROMOHEXANE

V. P. Golmov

In the previous papers [1,2,3,4,5] we reported the results of investigations of the interaction of sodio-malonic ester with dihalo derivatives of symmetrical structure (trimethylene bromide, tetra- and pentamethylene bromides, 2,5-dibromohexane, hexamethylene iodide, and a number of others).

A fairly large number of researches are known in which are described reactions between sodio-malonic (or sodio-acetoacetic) ester and dihalo derivatives of unsymmetrical structure (1,3-dibromobutane [6], 1,5-dibromohexane [7], etc.). The mechanism of these reactions has never been investigated, the literature therefore being lacking in any information on, for example, which of the two bromine atoms (attached to the primary or secondary carbon atom) is the first to enter into reaction with sodio-malonic ester.

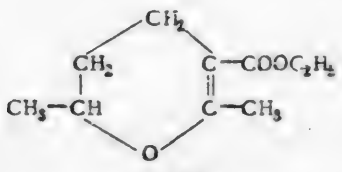
Only isolated conjectures about the course have been suggested. Thus, for example, Perkin, Jr. [7], in acting with sodio-acetoacetic ester on 1,5-dibromohexane in equimolar ratios, assigned the structure of (I) to the product without giving any proof:



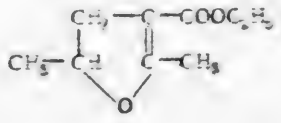
(I)

He assumed that the atom of bromine attached to the secondary carbon atom must be the first to enter into reaction.

In another research, however, the same author [8] reacted sodio-acetoacetic ester with 1,3-dibromobutane and obtained 2,6-dimethyl-5,6-dihydropropane-3-carboxylic ester (II). Lipp and Scheller [9] showed that in the action of sodio-acetoacetic ester on propylene bromide, 2-methyl-1-acetylcyclopropane-1-carboxylic ester and the ester of β-methyl-α,α'-diacetyladipic acid are formed, but also the ester of 2,5-dimethyl-4,5-dihydrofuran-3-carboxylic acid (III)

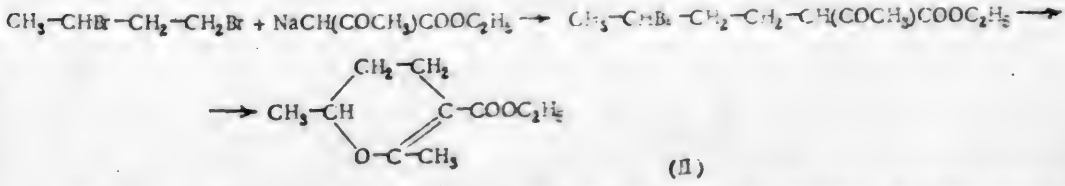


(II)



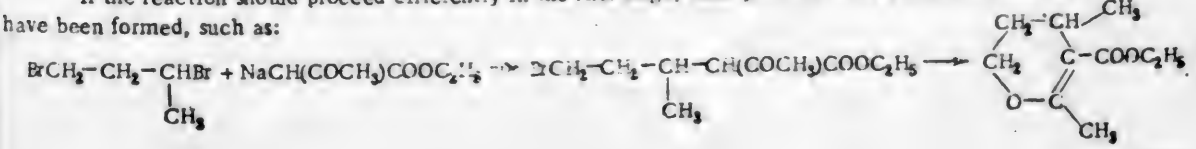
(III)

It is not difficult to see that the formation of these substances must be preceded by the formation of bromoalkylacetoacetic esters with the atom of bromine at the secondary carbon atom, for example



(II)

If the reaction should proceed differently in the first stage, then products with a different structure would have been formed, such as:



In this research we have investigated the action of sodio-malonic ester on 1,5-dibromohexane for the purpose of establishing which of the two atoms of bromine in the molecule of an unsymmetrical dihalo derivative is the first to react with sodio-malonic ester.

In this investigation an intermediate product was obtained in the shape of bromohexylmalonic ester which could be either ϵ-bromohexylmalonic ester (IV) or ϵ-bromo-α-methyl-amylmalonic ester (V).

In order to verify its structure, both the latter compounds were synthesized by another route, namely, by addition of HBr to ϵ-hexenylmalonic ester which was synthesized for this purpose by the action of sodio-malonic ester on 6-bromo-1-hexene (for compound IV), and by addition of HBr in presence of benzoyl peroxide to the previously [3] prepared α-methyl-δ-pentenylmalonic ester (for compound V):

$$CH_2=CH-CH_2-CH_2-CH_2-CH_2-CH(COOC_2H_5)_2 \xrightarrow{HBr} CH_2-CHBr-CH_2-CH_2-CH_2-CH_2-CH(COOC_2H_5)_2 \quad (IV)$$

$$CH_2=CH-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH(COOC_2H_5)_2 \xrightarrow[\text{benzoyl peroxide}]{HBr} CH_2Br-CH_2-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH(COOC_2H_5)_2 \quad (V)$$

The structure of both compounds was confirmed by the formation from them, by the action of sodium ethylate, of 1-methylcyclohexane-2,2-dicarboxylic acid ester.

The two prepared bromoesters differed fairly sharply in physical constants and behaved quite diversely under the action of sodium alcoholate.

Whereas ϵ-bromo-α-methyl-amylmalonic ester is converted into 1-methylcyclohexane-2,2-dicarboxylic ester in a yield of 70% of the theoretical when cyclized with the help of sodium alcoholate, ϵ-bromohexylmalonic ester in the same conditions is cyclized with a yield of only 5% of the theoretical. Only by working in very dilute solution was it possible to convert it into 1-methylcyclohexane-2,2-dicarboxylic ester in a yield of about 45% of the theoretical. In the latter case, a small amount of the ethyl ester of ϵ-ethoxyhexylmalonic acid is also formed.

The bromohexylmalonic ester prepared by the action of sodio-malonic ester on 1,5-dibromohexane is completely identical in its constants and behavior on cyclization with ϵ-bromohexylmalonic ester, and it is therefore extremely probable that it has the same structure.

EXPERIMENTAL

The 1,5-dibromohexane required for the research was prepared by the method of Perkin, Jr. [10], action of HBr on 1,5-hexanediol. The prepared starting material had b.p. 93-96° at 5 mm [11].

Action of Sodio-malonic Ester on 1,5-Dibromohexane

To a solution of alcoholate, prepared from 5.7 g (0.24 g-atom) metallic sodium and 75 ml absolute alcohol, was added 115 g (0.72 mole or three times more than the theoretically calculated amount) malonic ester, and then 59 g (0.24 mole) 1,5-dibromohexane. The mixture was heated to boiling on a bath for 6 hours; it was then cooled and water was added; the resultant oil was extracted with ether and the ether extract was washed with water and dried with calcined calcium chloride. The ether was then driven off and the residue fractionated in vacuum. The excess of malonic ester came over first (80° (5 mm) fraction), followed by a fraction with b.p. 153-180° (3 mm) consisting of bromohexenylmalonic ester in the form of a colorless oily liquid with the characteristic odor of a bromoalkyl malonic ester. A considerable residue remained in the flask. On redistillation this fraction boiled mainly at 160-161° (3 mm).

d_4^{20} 1.2073; n_D^{24} 1.4612. MR_D 73.45. $C_{15}H_{25}O_4Br$. Calculated: MR_D 73.31.

0.2360 g substance: 0.4192 g CO_2; 0.1472 g H_2O. 0.3472 g substance: 0.2003 g AgBr (Carius). Found %: C 48.44; H 6.92; Br 24.54. $C_{15}H_{25}O_4Br$. Calculated %: C 48.30; H 7.12; Br 24.69.

ϵ-Hexenyl Malonic Ester

To a solution of alcoholate, prepared from 10.4 g (0.45 g-atom) metallic sodium and 120 ml absolute alcohol, was added first 144 g (0.9 mole) [12] malonic ester and second 73 g (0.45 mole) 6-bromo-1-hexene (prepared by addition of HBr to 1,5-hexadiene [13]). The mixture was heated at the boil on a bath for 6 hours; after cooling, it was then poured into water acidified with hydrochloric acid; the reaction products were extracted

with ether and the ether extract was washed with water and dried with calcined calcium chloride; the ether was driven off and the residue subjected to fractional distillation in vacuum in a column. Malonic ester, b.p. 80° at 4 mm (74.5 g) first came over; the thermometer then rose rapidly and at 120-121° (4 mm) 80 g ϵ-hexenylmalonic ester came over (73.4% of the theoretical).

After a second distillation the product boiled at 114-115° (2 mm) and consisted of a colorless, almost odorless liquid.

d_4^{20} 0.9755; n_D^{20} 1.4390; MR_D 65.25. $C_{12}H_{22}O_4$. Calculated: MR_D 65.08.

0.2574 g substance: 0.6072 g CO_2; 0.2133 g H_2O. Found %: C 64.34; H 9.20. $C_{12}H_{22}O_4$. Calculated %: C 64.46; H 9.09.

12 g of the substance was saponified with a solution of 10 g KOH in 50 ml 95% alcohol with heating for 1½ hours. The liquid was then diluted with water, the alcohol was completely distilled off on a water bath, and the residue (cooled) was acidified with dilute H_2SO_4 and extracted 5 times with ether. The ether extract was dried with ignited calcium chloride and the ether distilled off to leave 8.9 g (96.5% of the theoretical) of crystalline ϵ-hexenylmalonic acid. After two recrystallizations from benzene it melted at 79°.

0.2042 g substance: 0.4352 g CO_2; 0.1368 g H_2O. Found %: C 58.12; H 7.44. $C_9H_{14}O_4$. Calculated %: C 58.06; H 7.53.

ϵ-Hexenylmalonamide was prepared by the action of aqueous ammonia (s.g. 0.88) on ϵ-hexenylmalonic ester at the ordinary pressure for several days, using the method of Demyanov and Telnov [14]. After recrystallization from water it melted at 195-196°.

0.1336 g substance: 14.4 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 15.09. $C_9H_{16}O_2N_2$. Calculated % N 15.21.

7.8 g ϵ-hexenylmalonic acid was heated under a reflux condenser on a bath of Wood's alloy at 180-200° until CO_2 ceased to come off. The 1-octene-8-carboxylic acid remaining after decarboxylation distilled at 234-238° (706 mm). The yield was 4.9 g or 83.1% of the theoretical.

d_4^{20} 0.9348; n_D^{20} 1.4430. MR_D 40.27. $C_9H_{14}O_2$. Calculated: MR_D 40.21.

0.2706 g substance: 0.6677 g CO_2; 0.2456 g H_2O. Found %: C 67.29; H 10.08. $C_9H_{14}O_2$. Calculated %: C 67.60. H 9.86.

1-Octene-8-carboxylamide was prepared by the usual method via the acid chloride by acting on the latter in solution in dry ether with gaseous ammonia. After recrystallization from chloroform it melted at 75-76°.

0.1080 g substance: 7.64 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 9.90. $C_9H_{15}ON$. Calculated %: N 9.92.

ϵ-Bromohexylmalonic Ester

Into 58 g (0.24 mole) ϵ-hexenylmalonic ester (cooled with snow and salt) was passed 22 g (0.27 mole) of moist [17] hydrogen bromide. The mixture was left at room temperature for 24 hours and then poured into water; the reaction product was separated, washed with water, dried with ignited calcium chloride, and distilled in vacuum, when the whole came over at 160-161° (3mm). Yield 72.5 g. or 92.1% of the theoretical.

d_4^{20} 1.2084; n_D^{20} 1.4619. MR_D 73.40. $C_{12}H_{21}O_4Br$. Calculated: MR_D 73.31.

0.3148 g substance: 0.5562 g CO_2; 0.2042 g H_2O. 0.3583 g substance: 0.2063 AgBr (Carius). Found %: C 48.19; H 7.21; Br 24.42. $C_{12}H_{21}O_4Br$. Calculated %: C 48.30; H 7.12 Br 24.69.

The substance is a colorless, heavy liquid with the odor of a bromoalkylmalonic ester.

ϵ-Bromo-α-methylamylmalonic Ester

To 42.5 g (0.17 mole) of α-methyl-δ-pentenylmalonic ester [3] was added 0.2 g benzoyl peroxide and about 20.0 g of dry HBr was introduced while cooling with ice and salt. The mixture was left at room temperature for 24 hours, then poured on to water; the lower layer was separated, washed with water, dried with ignited calcium chloride, and distilled in vacuum. Nearly the whole came over at 156-157° (3 mm). Yield 46 g, or 83.8% of the theoretical.

d_4^{20} 1.2143; n_D^{20} 1.4630; MR_D 73.34. $C_{13}H_{23}O_4Br$. Calculated: MR_D 73.31.

0.2164 g substance: 0.3820 g CO_2; 0.1382 g H_2O. 0.3938 g substance: 0.2258 g AgBr (Carius). Found %: C 48.15; H 7.10. Br 24.40. $C_{13}H_{23}O_4Br$. Calculated %: C 48.30; H 7.12; Br 24.69.

Cyclization of ε-Bromo-α-methylamylmalonic Ester

2.3 g (0.1 g-atom) metallic sodium was dissolved in 50 ml absolute alcohol and to the alcoholate solution was added (with cooling) 32.2 g ε-bromo-α-methylamyl-malonic ester. The initial concentration of the reacting substance was 1.3 molar. The mixture was heated on a bath at the boil for 4 hours and then cooled, poured into water; the reaction product was extracted several times with ether and the ether extract was washed with water, and dried with ignited calcium chloride; the ether was driven off and the residue was fractionated in vacuum to give 15.5 g with b.p. 116-117° (5 mm) and 5 g residue. The yield was 72.3% of the theoretical.

d_4^{20} 1.0312; n_D^{20} 1.4506; MR_D 63.14. $C_{13}H_{22}O_4$. Calculated: MR_D 63.34.

0.2728 g substance: 0.6435 g CO_2; 0.2244 g H_2O. Found %: C 64.36; H 9.13. $C_{13}H_{22}O_4$. Calculated %: C 64.47; H 9.09.

The substance was saponified with 20% alcoholic KOH for 1½ hours, after which the liquid was diluted with water and the alcohol distilled off. The residue, after cooling, was acidified with dilute sulfuric acid and repeatedly extracted with ether. The ethereal extract was dried with ignited calcium chloride and the solvent was driven off, leaving the dicarboxylic acid in the form of a thick oil which partly crystallized after lengthy standing in a desiccator over sulfuric acid. The crystals were drained, pressed on a porous plate and twice recrystallized from a small quantity of formic acid. M.p. 154-155°. According to Perkin [15], 1-methylcyclohexane-2,2-dicarboxylic acid melts at 147°.

0.1084 g substance: 0.2303 g CO_2; 0.0746 g H_2O. Found %: C 57.94; H 7.65. $C_9H_{14}O_4$. Calculated %: C 58.06; H 7.53.

The other portion of the 1-methylcyclohexane-2,2-dicarboxylic acid, immediately after isolation from the ethereal solution, was heated in Wood's alloy to 200° and transformed into cis-hexahydro-o-toluic acid, which, on distillation, boiled at 230-235° [16]. The latter was converted, via the acid chloride, into the amide which melted at 150-152° after two recrystallizations from dilute methyl alcohol [16].

Cyclization of ε-Bromohexylmalonic Ester

The experiments described below were performed both with ε-bromohexylmalonic ester prepared by addition of HBr to ε-hexenylmalonic ester and with the bromoester prepared by reaction of sodio-malonic ester with 1,5-dibromohexane. In both cases identical results were obtained.

First experiment. To a solution of alcoholate prepared from 1.6 g (0.07 g-atom) metallic sodium and 35 ml absolute alcohol was added 21.5 g (0.067 mole) ε-bromohexylmalonic ester. The initial concentration of the reacting substance was 1.26 molar. The mixture was heated at the boil on a bath for 5 hours, after which addition was made to it (with cooling) of water acidified with hydrochloric acid; the resultant oil was extracted with ether and the ethereal extract was washed with water and dried with ignited calcium chloride; the ether was distilled off. Vacuum distillation of the residue gave a total distillate of 0.8 g, boiling at 124-126° (6 mm). The residue in the flask was about 15 g viscous, dark oil which could not be distilled without decomposition. The 124-126° fraction was, as shown below, 1-methylcyclohexane-2,2-dicarboxylic ester. Yield 5% of the theoretical.

Second experiment. 16.2 g (0.05 mole) bromoester was added to a solution of alcoholate prepared from 1.15 g (0.05 g-atom) metallic sodium and 287 ml absolute alcohol. The initial concentration in this case was 0.17 molar. After heating at the boil on a bath for 5 hours, distillation of the greater part of the alcohol, and further working-up in the above-described manner, 3.8 g 1-methylcyclohexane-2,2-dicarboxylic ester with b.p. 125-131° (8 mm) was obtained (31.4% of the theoretical), as well as 2.2 g of a fraction coming over at 131-170° (8-9 mm). The residue in the flask was a fairly large amount of viscous, dark liquid.

Third experiment. In order not to excessively increase the volume of the reacting mixture, to the alcoholate solution prepared from 1.0 g (0.043 g-atom) metallic sodium and 250 ml absolute alcohol (heated to boiling) was added 14 g (0.043 mole) ε-bromohexylmalonic ester in 10 portions of 1.4 g each. After each addition the initial concentration of the reacting substance was 0.017 molar. After each addition the liquid was boiled on a bath for an hour. After working up as in the second experiment, vacuum fractionation gave 4.7 g (45.2 % of the theoretical) 1-methylcyclohexane-2,2-dicarboxylic ester with b.p. 124-131° (8 mm), also 1.5g of a fraction with boiling range 131-170°. The 124-131° fractions from the three experiments were combined and after a fresh distillation in vacuum the liquid boiled (mainly) at 110-114° (3 mm).

d_4^{20} 1.0296; n_D^{20} 1.4490; MR_D 63.11. $C_{13}H_{22}O_4$. Calculated: MR_D 63.34.

0.2692 g substance: 0.6385 g CO_2; 0.2262 g H_2O. Found %: C 64.69; H 9.33. $C_{13}H_{22}O_4$. Calculated %: C 64.49; H 9.12.

The ester of 1-methylcyclohexane-2,2-dicarboxylic acid was saponified with alcoholic KOH and the resultant 1-methylcyclohexane-2,2-dicarboxylic acid (a thick oil) was decarboxylated to form cis-hexahydro-o-toluic acid with b.p. 230-236°. The amide was prepared as above and after two recrystallizations from dilute methyl alcohol it had m.p. 151-152° [6].

The 131-170° fraction obtained in the second and third experiments was redistilled in vacuum to give about 2 g substance with b.p. 148° (3 mm).

The physical constants and the elementary analysis of this substance indicate that it is probably the ethyl ester of ϵ-ethoxyhexylmalonic acid, formed as a by-product during the action of sodium alcoholate on ϵ-bromohexylmalonic ester.

d_4^{20} 0.9871; n_D^{20} 1.4376; MR_D 76.53. $C_{15}H_{28}O_5$. Calculated: MR_D 76.42.

0.2451 g substance: 0.5619 g CO_2; 0.2092 g H_2O. Found %: C 62.52; H 9.67. $C_{15}H_{28}O_5$. Calculated %: C 62.50; H 9.72.

SUMMARY

1. Sodio-malonic ester reacts with 1,5-dibromohexane to give bromohexylmalonic ester as an intermediate product.

2. The structure of the latter was confirmed by synthesis of both of the possible bromohexylmalonic esters — ϵ-bromohexylmalonic ester and ϵ-bromo-α-methylamylmalonic ester — by addition of HBr to α-methyl-δ-pentenylmalonic ester.

3. A comparison of the physical constants of both bromoesters with the properties of the bromoester obtained by the action of sodio-malonic ester on 1,5-dibromohexane, also the behavior of these substances when cyclized with the help of sodium alcoholate, show that the bromoester formed by the action of sodio-malonic ester on 1,5-dibromohexane is ϵ-bromohexylmalonic ester.

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SYNTHESIS OF PARTIAL ACYLALS OF LACTIC ACID

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The conditions for synthesis of partial acylals from monocarboxylic acids and vinyl ethers were worked out by M. F. Shostakovsky and N. A. Gershtein [1]. Interaction of the starting components is effected without catalyst at a temperature above the boiling point of the reaction mass. This reaction is notable for its simplicity and proceeds in one step. Isolation of the products in the pure form only calls for a fractional distillation. The mechanism of formation of partial acylals by this method is represented by the equation:

$$CH_2{=}CHOR + R'COOH \rightarrow CH_2{=}CH{-}O{-}R \rightarrow CH_3CH(OCOR')OR.$$
$$\vdots$$
$$HOCOR'$$

The partial acylals are obtained in a yield of 61 to 84%.

The synthesis and properties of acylals of monocarboxylic acids have been adequately studied [2-6]. Acylals of hydroxy acids, as prepared by interaction of lactic acid with vinyl ethers, have been prepared and described by us for the first time.

Lactic acid contains two functional groups and may be expected to add on vinyl ethers both at the hydroxyl and the carboxyl. However, the reaction of vinylbutyl ether with lactic acid at 25-84° showed that the products obtained are the result of addition of the acid to the ether at the carboxyl and not at the hydroxyl [7]. Consequently, the formation of alkoxy-ethylidene lactates may be represented by the equation:

$$CH_2{=}CHOR + HOCOCHOHCH_3 \rightarrow CH_3CH(OR)OCOCHOHCH_3.$$

In the conditions of esterification of the carboxyl of lactic acid, another possibility is addition of the vinyl ether at the hydroxyl of this acid. Thus, when the ethyl ester of lactic acid was brought into reaction with vinylbutyl ether in an autoclave at 150-160°, a new product was formed according to the equation:

$$CH_3CHOHCOOC_2H_5 + H_2C{=}CHOC_4H_9 \rightarrow CH_3CH(OC_4H_9)OCHCOOC_2H_5.$$
$$\vdots$$
$$CH_3$$

Alkoxyethylidene-lactates are soluble in alcohols, acetone, benzene and dioxane. Butoxyethylidene-lactate is less stable toward water than the corresponding butoxy-ethylidene-propionate. The lower representatives of the partial acylals of lactic acid are hydrolyzed rapidly and completely on contact with water. This behavior is evidently associated with the hydrophilic properties of lactic acid. Ethoxy- and propoxy-ethylidene-lactates are readily soluble in water and easily hydrolyzed at room temperature. With rising molecular weight the solubility in water decreases; thus, butoxy-ethylidene-lactate is only soluble in 15 times the amount of water and after energetic shaking. The optimum conditions for synthesis of partial acylals of lactic acid are a temperature of 85-100° without a catalyst in an autoclave.

The alkoxyethylidene-lactates that we prepared possess the properties common to vinyl ethers and their derivatives. Increasing molecular weight of the acylal is accompanied by a rise in boiling point and coefficient of molecular refraction and by a fall in specific gravity (see table). The yield of lactates reaches 60%. The lactic acid is partially converted into lactide, while the vinyl ether hydrolyzes to alcohol and acetaldehyde. The structure of the prepared compounds was confirmed by hydrolysis and determination of the percentage of acetaldehyde and lactic acid. The hydrolysis proceeds according to the equation

$$CH_3CH(OR)OCOCHOHCH_3 \xrightarrow[H_2O]{H^+} CH_3CHO + ROH + CH_3CHOHCOOH.$$

Characteristics of Alkoxyethylidene-Lactates

No.	Formula	Gross formula	B.p.	n_D^{20}	d_{20}^{20}	d_4^{20}	MR_D found	MR_D calc'd	M found	M calc'd	% C found
I	$CH_3CHOCH(CH_3)COOC_2H_5$ (OC$_4$H$_9$)	$C_{11}H_{22}O_4$	105-106 (at 0.5mm)	1.4287	0.9596	0.9579	58.1	58.167	220.9	218.3	60.54
II	$CH_3CHOCOCHOHCH_3$ (OC$_2$H$_5$)	$C_7H_{14}O_4$	152-154	1.4100	1.0120	1.0102	40.0	39.498	163.4	162.2	51.85
III	$CH_3CHOCOCHOHCH_3$ (OC$_3$H$_7$)	$C_8H_{16}O_4$	166-167	1.4155	0.9835	0.9917	44.9	44.136	177.8	176.2	54.72
IV	$CH_3CHOCOCHOHCH_3$ (OC$_4$H$_9$)	$C_9H_{18}O_4$	188-189	1.4195	0.9700	0.9683	49.6	48.774	190.4	190.2	56.86
V	$CH_3CHOCOCHOHCH_3$ (OC$_5$H$_{11}$-iso)	$C_{10}H_{20}O_5$	70-74 (at 5mm)	1.4245	0.9672	0.9656	53.0	53.412	200.8	204.1	58.96
VI	$CH_3CHOCOCHOHCH_3$ (OC$_6$H$_{13}$)	$C_{11}H_{22}O_4$	81-82 (at 5mm)	1.4285	0.9656	0.9639	58.3	58.050	—	—	60.43
VII	$CH_3CHOCOCHOHCH_3$ (OC$_8$H$_{17}$)	$C_{13}H_{26}O_4$	93-96 (at 5mm)	1.4358	0.9484	0.9467	68.0	67.326	—	—	63.66
VIII	$CH_3CHOCOCHOHCH_3$ (OC$_6$H$_{11}$-cyclo)	$C_{11}H_{20}O_4$	86-88 (at 3mm)	1.4537	1.0677	1.0658	54.9	55.830	—	—	60.84

A study was later made of the interaction of lactic acid with isoamyl-, hexyl-, octyl- and cyclohexylvinyl ethers. Synthesis of lactates (V, VI, VII, and VIII) was accomplished without a catalyst under the influence of heat (85-100°), both at normal pressure and in an autoclave. The yield of products was 5 to 27%. The low yield of lactates is bound up with the properties of the vinyl ethers which react slowly and far from completely at 85-100°. On the other hand, rise of temperature to above 100° or performance of the reaction in presence of acid catalysts, leads to resinification and lowers the yield of lactates. The prepared lactates differ from the lower representatives of the series (I, II, III and IV) in being insoluble in water. Their hydrolysis proceeds under the influence of water, acids or alkalies at 100° and on prolonged heating in sealed ampoules; this process was utilized for establishing the structure of the lactates.

The described compounds are readily soluble in ethyl ether and acetone, less soluble in benzene and dioxane. After keeping for a long period (up to 3 months) the lactates are slowly hydrolyzed due to the action of atmospheric moisture. The slowness of water absorption is possibly correlated with the size of the radical (isoamyl, hexyl, octyl, cyclohexyl) which protects the free hydroxyl of lactic acid and makes it less hydrophilic. The partial acylals may be arranged in the following order of decreasing solubility in water:

$$CH_3CH(OC_2H_5)OCOR > CH_3CH(OC_3H_7)OCOR > CH_3CH(OC_4H_9)OCOR > \ldots CH_3CH(OC_8H_{17})OCOR$$

Whereas the first two members of the series have good solubility in water, butoxyethylidene-lactate is only soluble in 15 times its volume of water, while isoamyloxyethylidene-lactate and the higher members of the series are insoluble in water.

EXPERIMENTAL

1. Interaction of Ethyl Lactate with Vinylbutyl Ether

59 g ethyl lactate (b.p. 153-155°; n_D^{20} 1.4013; d_4^{20} 1.0310) and 50 g vinylbutyl ether (b.p. 93-94°; n_D^{20} 1.4025; d_4^{20} 0.7793) were heated in an autoclave for 8 hours at 150-160°. 102 g of a yellow liquid was discharged and on fractionation gave a substance with b.p. 102-106° (0.5 mm); n_D^{20} 1.4186; resinous residue 9.7 g; weight of material in trap 23.9 g.

The contents of the trap were treated with metallic sodium and then distilled at 145-147°; n_D^{20} 1.3980; d_{20}^{20} 0.8312; d_4^{20} 0.8297. The constants agree with those for acetaldehyde-ethylbutyl acetal. The ethyl alcohol for reaction

%C calc'd	%H found	%H calc'd
60.63	10.06	10.16
51.85	8.43	8.64
54.53	9.12	9.15
56.84	9.67	9.47
58.84	9.72	9.81
60.52	10.17	10.16
63.28	10.82	10.64
61.08	9.48	9.32

with vinylbutyl ether is probably formed by decomposition of the ethyl lactate. The yield of acetaldehyde-ethylbutyl acetal was 18.26 g (25% on the vinylbutyl ether).

0.1399 g substance: 18.27 g benzene: Δt 0.267°. 0.2575 g substance: 18.27 g benzene: Δt 0.495°. Found: M 146.26, 145.21. $C_8H_{18}O_2$. Calculated: M 146.224. 0.1005 g substance: 25 ml bisulfite: 17.7 ml 0.1 N I_2. 0.1153 g substance: 25 ml bisulfite: 15.4 ml 0.1 N I_2. For 25 ml bisulfite, 30.4 ml 0.1 N I_2 was consumed. Found %: acetal 91.89, 95.12.

The substance with b.p. 102-106° (0.5 mm) was carefully treated with metallic calcium and distilled; it was identified as butoxyethylidene-2-lacto-3-ethylate whose formula (I) and main constants are given in the table. Yield 63.6 g (58.3% of the theoretical).

Hydrolysis with determination of the percentage of acylal as acetaldehyde: 0.1207 substance: 25 ml bisulfite: 19.7 ml 0.1 N I_2. 0.1299 g substance: 25 ml bisulfite: 19.0 ml 0.1 N I_2. For 25 ml bisulfite was consumed 30.7 ml ml 0.1 N I_2. Found %: acylal 96.32, 97.53.

Hydrolysis with alcoholic KOH with determination of the percentage of acylal as acid: 0.2817 g substance: 13.6 ml 0.1 N HCl. 0.3015 g substance: 13.9 ml 0.1 N HCl. Found %: acylal 100.8, 100.7.

2. Interaction of Lactic Acid with Vinylethyl Ether

90 g lactic acid, previously purified through the magnesium salt [8], with m.p. 17-18° and b.p. 118-119° (12 mm), and 72 g vinylethyl ether (b.p. 36-36.5°; n_D^{20} 1.3780; d_4^{20} 0.7530, were charged into a flask cooled with tap water. After adding 0.1-0.2 g P_2O_5, the mixture froths violently and resinifies, the temperature rising to 42-45°. On lowering the temperature in the flask to 35°, this temperature is maintained for 1-1½ hours with a warm water bath. Over night the mixture in the flask separates into two layers: the upper one liquid, the lower one viscous (107 g and 50 g respectively). This viscous product had b.p. 118-119° (12 mm). Titration with alkali indicated that it was a monobasic acid.

0.2210 g substance: 24.5 ml 0.1 N NaOH. Found %: acid 99.88. Lactic acid recovered 45.2 g (50%).

Fractionation of the liquid gave: 1) b.p. 35-36°, n_D^{20} 1.3772 — 40 g; 2) b.p. 148-154°, n_D^{20} 1.4098 — 55 g; resinous residue 8 g.

The first fraction, after washing with water and drying, distilled at 36-36.5°; n_D^{23} 1.3780; d_4^{20} 0.7523. The constants agree with those of vinylethyl ether. Recovered from the reaction 36.1 g (50%).

0.0587 g substance: 25 ml bisulfite: 15.1 ml 0.1 N I_2 0.0769 g substance: 25 ml bisulfite: 10.1 ml 0.1 N I_2. For 25 ml bisulfite was consumed 30.1 ml 0.1 N I_2. Found %: ether 97.13, 98.76.

The second fraction, after careful treatment with a small amount of metallic calcium, distilled at 152-154° and consisted of ethoxyethylidene-lactate whose formula (II), constants and analysis are given in the table. Yield 52 g (32% of the theory).

Hydrolysis with determination of the percentage of acylal as acetaldehyde: 0.1168 g substance: 25 ml bisulfite: 16.7 ml 0.1 N I_2. 0.1264 g substance: 25 ml bisulfite: 15.4 ml 0.1 N I_2. For 25 ml bisulfite was consumed 30.7 ml 0.1 N I_2. Found %: acylal 97.20, 96.15.

Hydrolysis with determination of the percentage of acylal as acid: 0.2893 g substance: 18.0 ml 0.1 N HCl. 0.2368 g substance: 14.9 ml 0.1 N HCl. Found %: acylal 100.9, 101.98.

3. Synthesis of Ethoxyethylidene-Lactate (II) in the Autoclave

A mixture comprising 90 g lactic acid and 72 g vinylethyl ether was heated in an autoclave for 6 hours at 85-90°. 150 g yellow product was discharged and separated into two layers. From the upper liquid layer was isolated 27.4 g (38%) vinylethyl ether with b.p. 36-36.5°; n_D^{20} 1.3780, and 84.3 g (52%) ethoxyethylidene-lactate with b.p. 152-154°; n_D^{20} 1.4100. The viscous lower layer was vacuum-distilled to give: 1) 28.9 g (32%) with b.p. 117-119° (12 mm); 2) 8 g with b.p. 138-142° (8 mm), crystallizing at room temperature.

The first fraction, lactic acid, was identified by titration with alkali in presence of phenolphthalein.

0.2815 g substance: 31.4 ml 0.1 N NaOH; 0.2917 g substance: 22.6 ml 0.1 N NaOH. Found %: lactic acid 100.46, 100.9.

The second fraction, after 3 recrystallizations from ethyl alcohol, melted at 124°. The acicular crystals were moderately soluble in ethyl alcohol and ether. The data identify the substance as the D, L-lactide of lactic acid. Yield 4 g (5.5%). Literature data [8]: b.p. 142° at 8 mm, m.p. 124.5°.

7.283 mg substance: 13.342 mg CO_2; 3.700 mg H_2O. 5.635 mg substance: 10.320 mg CO_2 2.175 mg H_2O. Found %: C 49.99, 49.98; H 5.68, 5.51. $C_6H_8O_4$. Calculated %: C 50.00; H 5.56.

4. Interaction of Lactic Acid with Vinylpropyl Ether

The synthesis of propyxyethylidene-lactate (III) and the treatment of the reaction products were effected in the conditions of experiment 3. From 90 g lactic acid and 86 g vinylpropyl ether were obtained: propoxy-ethylidene-lactate 89.4 g (50.8%), vinylpropyl ether 34.5 g (40%) and lactic acid 30 g (33%).

5. Interaction of Lactic Acid with Vinylbutyl Ether

90 g lactic acid and 100 g vinylbutyl ether were charged into a flask. After introduction into the mixture of 0.1-0.2 g P_2O_5, the temperature was raised to 80-95° for 20 minutes while cooling with tap water. The mixture was then heated for 2 hours at 90°. 185 g was discharged. Fractionation gave: 1) 90-94°; n_D^{20} 1.4023 —5.5 g; 2) b.p. 187-191°; n_D^{20} 1.4200 —80 g; 3) b.p. 120-122° (14 mm); n_D^{20} 1.4415 —41.5 g; 4) b.p. 138° (7 mm), 6 g; the substance crystallized.

After washing with water and drying, the first fraction distilled at 93-94°; n_D^{20} 1.4028; d_4^{20} 0.7794. The data correspond to those for vinylbutyl ether. Recovered from the reaction 51 g (51%).

0.1009 g substance: 25 ml bisulfite; 10.4 ml 0.1 N I_2. 0.1202 g substance: 25 ml bisulfite; 7.4 ml 0.1 N I_2. For 25 ml bisulfite 30.4 ml 0.1 N I_2 was consumed. Found % ether: 99.26, 95.82.

The second fraction, after careful treatment with a little metallic calcium, distilled at 188-189° and was butoxyethylidene-lactate; its formula, constants and analysis are given in the table. Yield 75 g (40% of the theoretical)

Hydrolysis with determination of the acylal as acetaldehyde: 0.2003 g substance: 25 ml bisulfite; 10.2 ml 0.1 N I_2. 0.2019 g substance: 25 ml bisulfite; 10.0 ml 0.1 N I_2. For 25 ml bisulfite 30.3 ml 0.1 N I_2 was consumed. Found %: acetal 95.45, 95.66.

Hydrolysis with determination of percentage of acylal as acid: 0.1938 g substance: 10.2 ml 0.1 N HCl. 0.2015 g substance: 10.7 ml 0.1 N HCl. Found %: acylal 100.7, 101.04.

The third fraction was identified as lactic acid; the amount recovered was 41.5 g (46%). 0.2138 g substance: 23.8 ml 0.1 N NaOH. Found %: acid 100.38.

The fourth fraction, after recrystallization from ethyl alcohol, melted at 123-124°, in agreement with the m.p. of D,L-lactide [8]. Yield 4.8 g (6.6%).

6. Synthesis of Butoxyethylidene-lactate (IV) in an Autoclave

A mixture of 90 g lactic acid and 100 g vinylbutyl ether was heated for 6 hours at 85-95° in an autoclave. The mixture was worked up to give the following products: vinylbutyl ether 40.3 g (40%), b.p. 93-94°, n_D^{20} 1.4026, butoxyethylidenelactate 130.3 g (52.8%), b.p. 188-189°, n_D^{20} 1.4195; d_4^{20} 0.9684; lactic acid 32 g (35.5%), b.p. 120-122° (14 mm); D,L-lactide 4.4 g (6.1%), m.p. 124°.

7. Interaction of Lactic Acid with Vinylisoamyl Ether

The synthesis of isoamyloxyethylidene-lactate (V) and the working-up of the reaction products were performed in the conditions of experiment 3. From 90 g lactic acid and 114 g vinylisoamyl ether (b.p. 112°, n_D^{20} 1.4090) was obtained: 55.9 g (27.4%) isoamyloxyethylidene-lactate, 61 g (68%) lactic acid and 74 g (65%) vinyl-isoamyl ether.

8. Preparation of Hexyloxyethylidene-lactate

A mixture of 83.2 g vinylhexyl ether (b.p. 143.5°; n_D^{20} 1.4171; d_4^{20} 0.7970)and 60.5 g lactic acid (b.p. 121-122° at 14 mm) was heated for 10 hours in an autoclave at 85-95°. 134.6 g was discharged. Fractionation gave:

first fraction 54.7 g, b.p. 55-60° (8 mm), n_D^{20} 1.4145; second fraction 39.3 g, b.p. 91-142° (8 mm), n_D^{20} 1.4288. The viscous residue in the flask (49.7 g) was not investigated. After the first fraction had been treated with metallic sodium, it distilled at 143.5°, n_D^{20} 1.4170, d_4^{20} 0.7969, which corresponds to vinylhexyl ether.

The constants of the second fraction, after repeated distillation, corresponded to hexyloxyethylidene-lactate (VI). Yield 16.65 g or 11.6% of the theoretical.

Hydrolysis with determination of the percentage of acylal as acid: 0.7000 g substance: 32.5 ml 0.1 N HCl, 0.5700 g substance: 26.4 ml 0.1 N HCl. Found %: acylal 101.03, 101.11.

9. Preparation of Octyloxyethylidene-lactate

A mixture of 156 g vinyloctyl ether (b.p. 186-187°, n_D^{20} 1.4274, d_4^{20} 0.8028), and 90 g lactic acid was charged into a three-necked flask fitted with a mechanical stirrer, mercury seal and reflux condenser, and connected to a trap and a thermometer which reached to the bottom of the flask; the mixture was heated for 13 hours at 85-99° and acquired a dark-brown color; on standing it separated into two layers. The upper layer (liquid) was filtered off from the precipitate—lactic acid. The amount of lactic acid recovered was 80 g (90%). Distillation of the filtrate in a current of dry nitrogen gave: first fraction, 60 g, b.p. 50-104° (5 mm), n_D^{20} 1.4280; second fraction, 19.5 g, b.p. 105-109° (5 mm), n_D^{20} 1.4323; third fraction, 18.9 g, b.p. 110-132° (5 mm), n_D^{20} 1.4325; fourth fraction, 39.0 g, b.p. 133-143° (5 mm), n_D^{20} 1.4365.

After treatment with metallic sodium the first fraction was distilled at normal pressure: b.p. 185-187°; n_D^{20} 1.4275. The substance is identical with vinyloctyl ether. Amount recovered 52.5 g (33%).

Fractions 2,3 and 4 were combined. Repeated vacuum distillation in a current of dry nitrogen gave 12.6 g (5.1%) octyloxyethylidene-lactate (VII), whose constants are given in the table.

Hydrolysis with determination of the percentage of acylal as acid: 0.6532 g substance: 26.7 ml 0.1 N HCl. 0.7586 g substance: 30.9 ml 0.1 N HCl. Found %: acylal 100.6, 100.4

10. Preparation of Cyclohexyloxyethylidene-lactate

A mixture of 126 g vinylcyclohexyl ether (b.p. 147-148°, n_D^{20} 1.4546) and 90 g lactic acid was heated for 7 hours to 75-90° (different from the conditions in experiment 9). The reaction mixture was worked up to give: 11.5 g (5.3%) cyclohexyloxyethylidene lactate (VIII), 107 g vinylcyclohexyl ether (85%) and 80 g (89%) lactic acid.

SUMMARY

A description is given for the first time of the interaction of ethyl lactate with vinylbutyl ether and of the interaction of lactic acid with the following vinyl ethers: ethyl, propyl, butyl, isoamyl, hexyl, octyl and cyclohexyl.

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THE REACTION BETWEEN ISOPROPYLMAGNESIUM CHLORIDE AND METHYL CHLOROFORMATE

G. A. Razuvaev and Yu. A. Oldekop

The reactions of esters of chloroformic acid with RMgX have been little studied in the past. V. K. Matsurevich [1] prepared triethylcarbinol and tripropylcarbinol from chloroformic ester and the appropriate RMgX. Zh. L. Iotsich [2] prepared the unsaturated alcohol, triallylenecarbinol, by reaction between chloroformic ester and allylenemagnesium bromide. Thus, the reaction between alkylmagnesium halides and an ester of chloroformic acid usually gives the corresponding tertiary alcohol.

In the investigation of several syntheses with RMgX it was shown that in the case of branched radicals, for example isopropyl, tert.-butyl and certain others, the main reaction of formation of tertiary alcohol is accompanied by another reaction involving reduction of the carbonyl compound. In some cases the normal formation of the corresponding tertiary alcohol is completely overshadowed by the reduction reaction [3]. This form of the reaction has been mainly studied with aldehydes, ketones and esters. As far as we know, transformations of this type have not been studied with chloroformic esters.

We have investigated the reaction between isopropylmagnesium chloride and methyl chloroformate. The components were in the ratio of 1 mole isopropylmagnesium chloride to 0.3 mole ester, i.e., the ratio most favorable to the formation of a tertiary alcohol.

The main products isolated from the reaction mixture, however, were diisopropylcarbinol and methyl isobutyrate. The tertiary alcohol – triisopropylcarbinol – could not be isolated. Consequently the main direction of the reaction is a reduction. The most probable mechanism of the reaction is that of Houben: formation of methyl isobutyrate as an intermediate which reacts with isopropylmagnesium chloride to form diisopropyl ketone, and the latter is reduced to diisopropylcarbinol in the reaction conditions.

We confirmed the formation of diisopropyl ketone from methyl isobutyrate and isopropylmagnesium chloride by a specially designed experiment.

EXPERIMENTAL*

Reaction of methyl chloroformate with isopropylmagnesium chloride. To the organomagnesium compound prepared from 24 g magnesium and 78.5 g (1.0 mole) isopropyl chloride was added dropwise, with cooling, over a period of 1 hour 28.5 g (0.3 mole) methyl chloroformate.

The reaction mixture was left for 2 hours, after which it was decomposed with dilute hydrochloric acid (1:10). The ether layer was washed with 10% sodium carbonate solution and dried over anhydrous sodium sulfate. After the ether had been driven off, the residue of 33 g was fractionated in a Vigreux column (35 cm long).

Fractions: 40-78°, 9.2 g; 78-92° 5.6 g; 94-134° 0.9 g; 135-141°, 3.9 g; 142-182° 1.2 g; 182-186°, 3.1 g, residue, 2.7 g.

For analytical purposes the following fractions were obtained by a second distillation: I 89-94°; II 137-141°, III 183-186°.

The first fraction with b.p. 89-94° consisted of methyl isobutyrate. No active hydrogen was found. Saponification gave isobutyric acid; m.p. of its anilide 98° (literature: 105°). The N-benzylamide of isobutyric acid was also prepared with m.p. 86.4°; it did not depress the melting point in admixture with an authentic specimen of the benzylamide of isobutyric acid. The yield of methyl isobutyrate, calculated on the methyl chloroformate taken, is 18.2%.

* Z. N. Zudina and Yu. A. Sorokin participated in the experimental work.

The second fraction with b.p. 137-141° consisted of diisopropylcarbinol.

d_4^{20} 0.8302, n_D^{20} 1.418; MR_D 35.3, calculated 36.1.

Found %: OH 14.1, 13.8; M 115.2, 115.7. $C_7H_{16}O$. Calculated %: OH 14.6; M 116.

Found %: C 71.5; H 14.0. $C_7H_{16}O$. Calculated %: C 72.3; H 13.7.

The substance was benzoylated by the Schotten-Baumann reaction and subjected to combustion.

Found %: C 75.8; H 9.4. $C_{14}H_{20}O_2$. Calculated %: C 76.3; H 9.1.

The yield of diisopropylcarbinol, calculated on the methyl chloroformate taken, was 28.3%.

Third fraction with b.p. 183-186°; d_4^{20} 0.8965; n_D^{20} 1.424. Found %: OH 7.5. This fraction was not further investigated.

Reaction between methyl isobutyrate and isopropylmagnesium chloride. The organomagnesium synthesis in the usual conditions with 5.6 g magnesium, 18 g isopropyl chloride and 10 g methyl isobutyrate gave a liquid from which diisopropyl ketone could be isolated. Preparation was carried out of the 2,4 dinitrophenylhydrazone with m.p. 95° and of the semicarbazone with m.p. 160°, in agreement with the literature data for these derivatives.

SUMMARY

1. Among the products of reaction of isopropylmagnesium chloride with methyl chloroformate were found diisopropylcarbinol and methyl isobutyrate. A tertiary alcohol could not be detected.

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INTERACTION OF SUBSTANCES CONTAINING ACTIVE METHYLENE GROUPS WITH DIAZO COMPOUNDS

A. A. Kharkharov

In organic chemistry a large number of compounds are encountered which are characterized, in comparison with saturated hydrocarbons, by very high lability of the methyl groups.

These compounds condense with carbonyl compounds (aldehydes and ketones), esters and anhydrides of carboxylic acids, and nitroso compounds; they also exchange the hydrogen of their methyl groups for deuterium and alkali metals [1-14].

We established for the first time that some members of this type of compounds are also capable of coupling with aromatic diazo compounds with formation of unusual azo dyes [15-19]

$$R{-}CH_3 + XN_2R_1 \longrightarrow R_1{-}CH_2{-}N{=}N{-}R_1 + HX$$

or

$$R{-}CH_3 + XN_2R_1 \longrightarrow R{-}CH{=}N{-}NH{-}R_1 + HX$$

This reaction was found to necessitate a higher activity of the methyl group than is required for condensation with carbonyl and nitroso compounds [16].

It was established that the requisite mobility of the hydrogens of the methyl group may be guaranteed by directly linking it with heterocyclic residues or with residues of aromatic compounds containing electrophilic substituents in the ortho and para- positions to the methyl group [15-19]. In the latter case the requisite activity of the methyl group is only achieved by introducing into the molecule several substituents with greater attractive power for electrons.

Thus, toluene and its derivatives containing nucleophilic substituents (for example xylenes) do not react with diazo compounds through the methyl group. Also incapable of undergoing this reaction are derivatives of toluene containing weak electrophilic groups: $-SO_3H$, $-COOH$, $-COR$ [19, 20]. It was found that only three nitro groups in the ortho- and para- positions impart to toluene the ability to couple with diazo compounds [19]. All other electrophilic substituents exert an inadequate effect.

From what has been said it follows that electrophilic substituents which increase the lability of the hydrogens of the methyl group can only endow these compounds with the ability to undergo azo coupling if they are conjugated with the methyl group and if they possess a sufficiently strong attractive power for the electrons of other atoms.

The increased lability of the hydrogen atoms of methyl groups due to redistribution of the electronic densities in the conjugated system under the influence of electrophilic atoms or groups is represented as follows:

$$H_3{\equiv}\overset{\curvearrowright}{C}{-}\overset{|}{C}{=}\overset{\curvearrowright}{}$$

We have shown that nucleophilic groups, in contrast to electrophilic groups, lower the lability of the hydrogens of methyl groups. Thus, the introduction into 2,4,6-trinitrotoluene of one more methyl group deprives it of the ability to react with diazo compounds [19].

In work with methylpyridines and methylacridines we established that the α- and γ-derivatives of some heterocyclic compounds are so active that they are capable of azo-coupling even in the absence of electrophilic substituents [15-18].

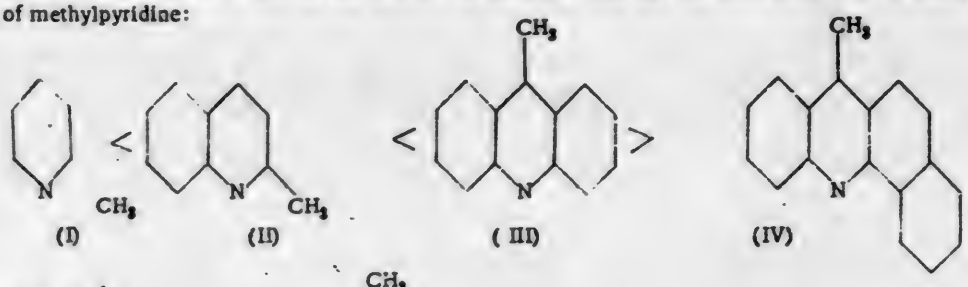
It was subsequently shown that this was also the case with benzo derivatives of methylacridine [22] and with methylpyrimidines [23].

The activity of unsubstituted 9-methylacridine toward diazo compounds is considerably higher than that of 2,4,6-trinitrotoluene. Whereas the latter compound does not couple even with such highly reactive compounds as p-sulfodiazobenzene, 9-methylacridine readily reacts not only with p-sulfodiazobenzene but also with weakly active diazo compounds containing several nucleophilic substituents, for example with 2,5-dimethoxy-4-phenylaminodiazobenzene.

The explanation of this phenomenon (on the basis of the scheme presented above) must be sought in the fact that the nitrogen of the heterocycle conjugated with the methyl group tends to increase its electronic density at the expense of both the inductive effect (according to its position in the Mendeleev system) and the conjugation effect. In other words, the heteroatom functions as a very strong electrophilic substituent. To this it is only necessary to add that the lability of the hydrogen atoms of the methyl groups is strongly influenced by the interaction of the three pairs of π-electrons of the benzene rings as well as, in particular, of the hetero rings.

The adduced experimental data are fully consistent with the theory—extensively developed by A. N. Nesmeyanov [21]—of the conjugation of the σ-electrons (σ-conjugation), and they must be regarded as a particular case of this phenomenon.

The effect of condensed aromatic rings on the activity of methyl groups may be illustrated with reference to benzo derivatives of methylpyridine:



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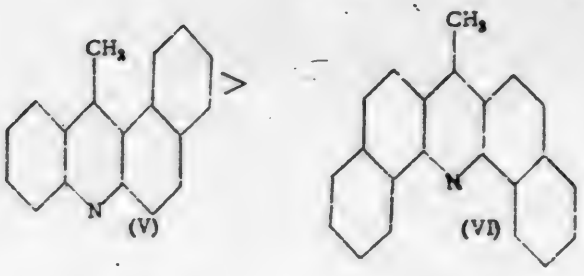
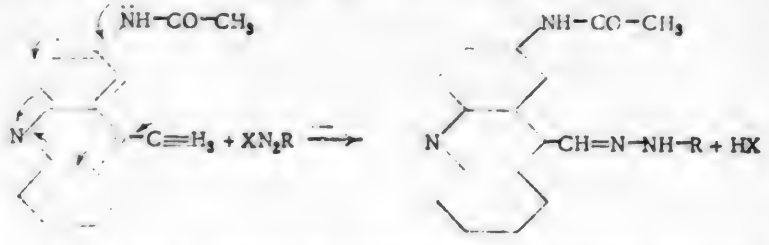


The successive increase in the mobility of the hydrogen in compound (II) and especially in compound (III) in comparison with (I) is due to supplementary interaction of the electrons of the methyl groups with the benzene rings. The fall in this mobility on passage from (III) to (V!) [22] is evidently due to the naphthalene nuclei possessing a less pronounced aromatic character and, consequently a weaker electrophilic character than the benzene rings. Hence, the attraction of the σ-electrons will be the weaker the larger the number of naphthalene nuclei in the compound.

This research also shows that in contrast to 2,4,6-trinitrotoluene, where the introduction of only one weakly nucleophilic substituent (a methyl group) deprives it of the ability to undergo azo coupling, the introduction in the 2-position to the acridine nitrogen of 9-methylacridine of the acetylamino group (much more strongly electron-repelling) does not deprive it of the ability to interact with diazo compounds:



It was found, however, that also in this case the introduction of a nucleophilic substituent into the molecule lowers the reactivity of the methyl group.

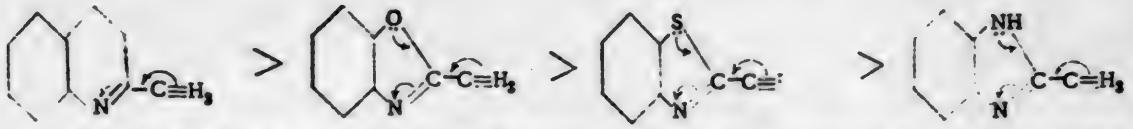
Whereas 9-methylacridine readily couples with nearly all aromatic diazo compounds, 2-acetylamino-9-methylacridine interacts only with the most active of these. It reacts slowly with phenyldiazonium, rather more

quickly with p-nitrophenyldiazonium, and does not react at all with p-methoxyphenyldiazonium.

From what has been said it follows that the heterocyclic nitrogen atom located in the α and γ-positions to the methyl group is so strongly activated by the latter that the compound retains the ability to couple even when the activating action of the heteroatom is reduced by the introduction of nucleophilic groups into its molecule.

The arylhydrazones of 2-acetylamino-9-acridine aldehyde that we prepared by the diazo reaction differ from the corresponding arylhydrazones of 9-acridine aldehyde by the position of their main absorption bands which are in the short-wave region of the spectrum (Fig. 1).

Previously, we had shown [16] that heterocyclic compounds of the type of quinaldine, 2-methylbenzoxazole, 2-methylbenzothiazole and 2-methylbenzimidazole may be arranged in the following order in respect of the activity of their methyl groups:



The fact that the head of this series is 2-methylbenzimidazole may be accounted for by the nitrogen atom of the $-\ddot{N}H-$ group, by virtue of its position in the periodic system of the elements, tending more strongly than the $-\ddot{S}-$ atom and the $-\ddot{O}-$ atom to reduce its electronic density at the expense of the conjugative effect with the α-carbon, so that the ionization tendency of the hydrogen is reduced. The transition of these compounds into the onium state, however, leads to heightened activity of their methyl groups [16].

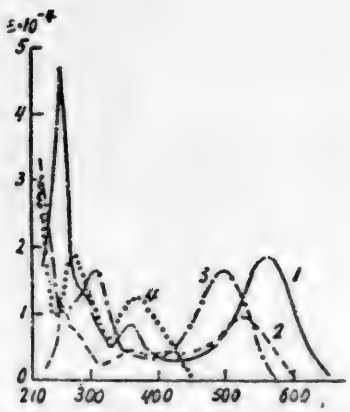


Fig. 1. Curves of absorption spectra. 1 - 9-acridine aldehyde phenylhydrazone; 2 - 9-acridine aldehyde p-nitrophenylhydrazone; 3 - 2-acetylamino-9-acridine aldehyde phenylhydrazone; 4 - 2-acetylamino-9-acridine aldehyde p-nitrophenylhydrazone (all in 0.2 N alcoholic HCl).

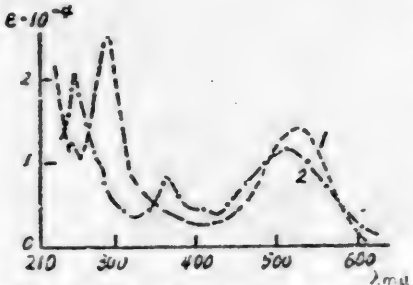
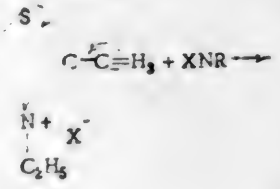
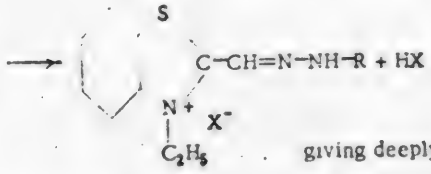


Fig. 2. Curves of absorption spectra. 1 - Cation of 1-ethyl-4'-nitrophenyl-2-benzothiazolealdehyde; 2 - cation of 10-ethyl-4-nitrophenylhydrazone of 9-acridinealdehyde (both in alcohol).

In this investigation we illustrate this thesis by reference to the previously uninvestigated interaction of 2-methylbenzothiazole ethoiodide with diazo compounds.

Unlike methylbenzylimidazole and methylbenzothiazole, which are incapable of coupling, the ethoiodide derivative of the latter readily enters into reaction with diazo compounds:





giving deeply colored dyes (Fig. 2).

EXPERIMENTAL

Preparation of 2',5'-Dimethoxy-4-phenylaminophenylhydrazone of 9-Acridinealdehyde

1.4 g 2,5-dimethoxy-4-aminodiphenylamine was diazotized at −5° with 0.4 g sodium nitrite in a solution of 6 ml water and 2ml 37% hydrochloric acid. The filtered diazo solution was added dropwise in the course of an hour to 18 g 9-methyl-acridine and 5 g crystalline sodium acetate dissolved in 24 ml 80% acetic acid. The reaction mass was kept at room temperature for 40 hours; it was then diluted with 60 ml water and filtered from the precipitate. The latter was washed with water, with 0.5% acetic acid and again with water; it was then treated with 5% ammonia,

thoroughly washed with water and dried at 70-80°. Yield of unpurified product 2.2 g (45% of the theoretical).

After recrystallization from a mixture of alcohol and pyridine, the product had m.p. 141°. The dark-red powder is insoluble in water, soluble in alcohol (brown solution) and in acetic acid (greenish-blue coloration).

Maxima of absorption bands in 0.2 N alcoholic HCl: $\lambda_1 = 258$ mμ, $\epsilon_1 = 5.12 \cdot 10^4$; $\lambda_2 = 360$ mμ, $\epsilon_2 = 1.68 \cdot 10^4$; $\lambda_3 = 630$ mμ, $\epsilon_3 = 1.9 \cdot 10^4$.

0.1225 g substance: 13.3 ml N_2 (21°, 760 mm). Found %: N 12.60. $C_{23}H_{16}O_2N_4$. Calculated %: N 12.50.

Preparation of the Phenylhydrazone of 2-Acetylamino-9-acridinealdehyde

2.35 g freshly distilled aniline was diazotized at 0° with 1.8 g sodium nitrite in a solution of 17 ml water and 12.5 ml 37% hydrochloric acid.

Two-thirds of the solution of the diazo compound was added over a period of 6 hours to a solution of 6.3 g 2-acetylamino-9-methylacridine, 150 ml glacial acetic acid and 20 g crystalline sodium acetate. The reaction mass was left for 20 hours. Addition was then made to it over a period of 2 hours of the remaining one-third of the diazo solution (the solution of diazo compound was freshly prepared). After 24 hours the reaction mixture was partly neutralized with aqueous ammonia while cooling. The precipitate was filtered off and washed first with water, then with 0.5% acetic acid and again with water; it was then treated with 5% ammonia solution, washed with water and dried at 50-60°. Yield of unpurified product 5.8 g (65.9% of the theoretical).

The dark-brown powder (from ethyl alcohol) had m.p. 111°. The product is insoluble in water; it dissolves in alcohol with a brownish-yellow, and in glacial acetic acid with a brownish-red color.

Absorption maxima in 0.2 N alcohol HCl: $\lambda_1 = 314$ mμ, $\epsilon_1 = 1.54 \cdot 10^4$; $\lambda_2 = 512$ mμ, $\epsilon_2 = 1.64 \cdot 10^4$.

0.1278 g substance: 16.7 ml N_2 (18°, 766 mm). Found %: N 15.41. $C_{23}H_{18}ON_4$. Calculated %: N 15.82.

Preparation of p-Nitrophenylhydrazone of 2-Acetylamino-9-acridinealdehyde

3.5 g p-nitroaniline was diazotized at −5 to −7° with 1.8 g sodium nitrite in solution in 15 ml 37% hydrochloric acid and 26 ml water. The prepared diazo solution was added in the course of 1½ hours to 6.3 g 2-acetylamino-9-methylacridine, 25 g crystalline sodium acetate in 100 ml water. The reaction mass was left for 17 hours. The precipitate was washed with water, with 0.5% acetic acid and again with water. The precipitate was then treated with 5% ammonia, filtered, and washed with water before drying at 50-60°. Yield of unpurified product 5.5 g (55% of the theoretical). Brownish-yellow powder with m.p. 178° (from alcohol). The product is insoluble in water; it dissolves in alcohol with a brownish-yellow and in acetic acid with a yellow color.

Absorption maxima in 0.2 N alcoholic HCl: $\lambda_1 = 222$ mμ, $\epsilon_1 = 3.0 \cdot 10^4$; $\lambda_2 = 278$ mμ, $\epsilon_2 = 1.84 \cdot 10^4$; $\lambda_3 = 375$ mμ, $\epsilon_3 = 1.24 \cdot 10^4$.

0.1004 g substance: 14.5 ml N_2 (17°, 764 mm). 0.1210 g substance: 18 ml N_2 (15°, 758 mm). Found %: N 17.08, 17.64. $C_{22}H_{17}O_3N_5$. Calculated %: N 17.54.

Preparation of ω-(o-Nitrobenzeneazo)-2,4,6-trinitrotoluene

2.3 g 2,4,6-trinitrotoluene was dissolved with energetic stirring in 50 ml pyridine, and to the red solution was added dropwise a previously prepared solution of p-nitrodiazobenzene (from 1.38 g p-nitroaniline), partly neutralized beforehand with sodium carbonate. The mass was stirred for 16 hours, after which it was poured onto a mixture of 45 ml 37% hydrochloric acid and 100 g ice. The resultant brown mass was filtered; the precipitate was triturated in a mortar with concentrated hydrochloric acid; the suspension was filtered; the precipitate was washed with water, then with alcohol, and dried at 40-60°. Yield of unpurified product 4.1 g (86% of the theoretical). After purification by elimination of starting materials with alcohol and recrystallization from glacial acetic acid, the melting point rose to 177°.

The water-insoluble brownish-red powder dissolved in 95% sulfuric acid with a violet coloration (λ_{max} −550 mμ). When the sulfuric acid solution was diluted with water, the product separated in the form of red flocs. It is soluble in alcohol, ether, acetone and glacial acetic acid; insoluble in gasoline and carbon tetrachloride.

0.0853 g substance: 16.4 ml N_2 (18°, 764 mm). Found %: N 22.51. $C_{13}H_8O_8N_6$. Calculated %: N 22.34.

Product of Coupling of α-Methylimidazole with Diazotized p-Nitroaniline

To a solution of 1 g α-methylimidazole and 10 g sodium acetate in 50 ml acetic acid was added over a period of 2 hours a previously prepared solution of the diazo compound from 1.38 g p-nitroaniline. The reaction mass was kept from 20 hours. The dark-brown precipitate was filtered off, washed with water, treated with dilute ammonia, washed with water and dried at 50-60°. Yield of unpurified product (m.p. 120°), 1.48 g (64% of the theoretical. After recrystallization from alcohol the m.p. was 129°.

The brown powder had m.p. 129-130° after recrystallization from methyl alcohol. The product does not dissolve in water; it dissolves in alcohol and acetic acid with a brownish-yellow color. Maxima of absorption bands: $\lambda_1 = 280$ mμ, $\epsilon_1 = 2.75 \cdot 10^4$; $\lambda_2 = 390$ mμ, $\epsilon_2 = 2.2 \cdot 10^4$.

0.0878 g substance: 23.2 ml N_2 (22°, 758 mm). Found %: N 30.49. $C_{10}H_9O_2N_5$. Calculated %: N 30.30.

Preparation of ω-(p-Nitrobenzeneazo)-α-methylpyridine

1.38 g p-nitroaniline was diazotized with 0.7 g sodium nitrite in solution in 6 ml hydrochloric acid and 11 ml water. Over a period of 1 hour the diazo solution was added to a mixture of 1.5 g α-methylpyridine with b.p. 129-130°, 50 ml 80% acetic acid and 10 g crystalline sodium acetate. After standing for 30 hours, the precipitate was filtered off, washed with water, then with 5% ammonia and finally with water before drying at 45-50°. Yield of unpurified product 1.4 g (58% of the theoretical). Yellow powder with m.p. 92° (from methyl alcohol). The product is soluble in alcohol and acetic acid; insoluble in water.

0.1086 g substance: 22.1 ml N_2 (22°, 756 mm). Found %: N 23.42. $C_{12}H_{11}O_2N_4$. Calculated %: N 23.14.

Preparation of ω-(p-nitrobenzeneazo)-3,5-dicarboxy-2,6-dimethylpyridine

1.38 g p-nitroaniline was diazotized with 0.7 g sodium nitrite in a solution of 6 ml 37% hydrochloric acid and 11 ml water. The resultant diazo solution was added over a period of 1 hour to a mixture of 2.4 g of the disodium salt of 2,6-dimethylpyridine-3,5-dicarboxylic acid, 40 ml 80% acetic acid and 10 g crystalline sodium acetate. After 20 hours' standing, the precipitate was filtered off, washed with water and dried at 50-60°. Yield of unpurified product 3.25 g (94% of the theoretical).

The yellowish-brown, water-insoluble powder is soluble in alcohol with a brownish-yellow color and in acetic acid with a yellow color. After purification with the help of acetic acid, the product had m.p. 174°. Maxima of the absorption bands of the alcoholic solutions: $\lambda_1 = 280$ mμ, $\epsilon_1 = 1.91 \cdot 10^4$; $\lambda_2 = 400$ mμ, $\epsilon_2 = 1.52 \cdot 10^4$.

0.1085 g substance: 15.1 ml N_2 (23°, 763 mm). Found %: N 16.10. $C_{15}H_{12}O_6N_4$. Calculated %: N 16.28.

SUMMARY

1. Azo-coupling at the methyl group was a logical development of the earlier work of A. E. Porai-Koshits on the lability of the hydrogen atoms of organic compounds.

2. It was established that the lability of the hydrogens of the methyl group necessary for the azo-coupling reaction can be secured by direct linkage to the methyl group of heterocyclic residues or of residues of aromatic compounds containing electrophilic substituents in the ortho- and para- positions to the methyl group (σ-conjugation).

3. It was shown that residues of pyridine, quinoline, acridine, benzoacridines and dibenzoacridines and other similar heterocycles, connected through the α- and σ-positions with the methyl groups, possess an exceptionally intense electrophilic action. They more strongly increase the mobility of the hydrogen of the methyl groups linked to them than do the aromatic residues.

4. It was established that, in contrast to the action of electrophilic substituents which, when in conjugation with the methyl group increase the lability of the latter's hydrogens, nucleophilic substituents lower the activity of the methyl group in its reactions with carbonyl, nitroso and diazo compounds.

5. New experimental results are presented which confirm our previous observation that the transition of a hetero atom into the onium state enhances its electrophilic properties. This transition is accompanied by increased mobility of the hydrogens of the methyl groups which are conjugated with the heteroatom.

6. The products of coupling with some diazo compounds of substances containing active methyl groups are described: α-methylpyridine, 2,6-dimethyl-pyridine-3,5-dicarboxylic acid; α-methylimidazole; 2,4,6-trinitrotoluene; 9-methylacridine; and 2-acetylamino-9-methylacridine.

7. The absorption curves are plotted of substances obtained by coupling with p-nitrodiazobenzene and diazobenzene of alkyl halide compounds of 2-methylbenzothiazole and 9-methylacridine, also nonalkylated 9-methylacridine and its 2-acetylamino derivative.

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THE SULFONATION REACTION

XXXII. ISOMERIZATION OF NAPHTHALENE DISULFONIC ACIDS

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Sulfonation of naphthalene gives 6 isomeric disulfonic acids. At a certain temperature and in water containing sulfuric acid, some isomers may be transformed into others. The process may proceed in the direction of formation of certain isomers to the end or to the setting-up of equilibrium states between them [1].

The phenomenon of reciprocal transition of naphthalene disulfonic acids was observed by Ebert and Merz [2], who noted the transformation of the 2,7-disulfonic acid into the 2,6-isomer at 160°. According to Fierz-David and Hasler [3], up to 27 % of the 2,6-disulfonic acid is obtained at 160°. Isomerization of the 1,5-acid starts below 100°, and it completely disappears from the sulfonic acid mixture after 8 hours at 130°. About 20% of 2,6-isomer is formed when the 1,5- or the 1,6-disulfonic acid is heated with 93% sulfuric acid for 8 hours at 160°. Heating of the 2,6-acid in these conditions leads to formation of the 2,7- and 1,6-isomers. Heid [4] heated the 2,7-isomer in 95% sulfuric acid at 160° and found up to 42% 2,6-acid in the mixture, but his analytical method was very inaccurate. Ambler, Lynch and Scanlan [5] heated the 1,5- and 1,6-isomer. at 120° and found the 2,7-isomer in the mixture. After 6 hours at 140°, the 1,6-isomer is almost completely isomerized, mainly to 2,7-isomer.

At 160° the 1.5- and 1,6-acids almost completely change into 2,6- and 2,7-acids. Vorozhtsov and Chuksanova [6] found that sulfonation of naphthalene at 160° gives the following isomers in the order of their yields: after 5 minutes 1,6- and 1,7-; after 30 minutes 1,6-, 2,6-, 2,7-, 1,7-; after an hour 1,7-, 1,6-, 2,7-, 2,6-; after 2 hours 2,7-, 1,7-, 2,6-.

On the basis of the above data it is impossible to detect any regularity in the isomerization of the disulfonic acids. Most chemists are of the opinion that the mechanism of rearrangement consists in hydrolysis of the sulfonic acid and in resulfonation of the products of hydrolysis. The sulfonic acids more stable to hydrolysis then preponderate. In a number of cases the possibility of intramolecular rearrangement is not rejected [6, 7].

On the basis of observations of the velocity of hydrolysis of naphthalene disulfonic acids and of the velocity of sulfonation of monosulfonic acids, Lantz [8] considers that 2,6- and 2,7-disulfonic acids are present in identical quantities in the sulfonated mixture. Heating of 2,6- and 2,7-disulfonic acids in sulfuric acid for 24 hours at 170° leads to an equilibrium state between equal parts of the 2,6- and 2,7- acids. Lantz indicates the possiblity of formation of the 1,6-isomer in addition. On isomerization, however, of the 1,6-acid at 100 - 130° the 2,6-isomer was observed to accumulate rapidly and the 2,7-isomer slowly, and this prompted the author to assume the presence of a new isomer, apparently the 1,7-acid. Heating of the 1,5-acid at 100° transforms it into the 1,6-isomer which, in turn, leads to 2,6- and 2,7-isomers.

It is necessary to remember that many experiments were performed by Lantz at a temperature and concentration of sulfuric acid such that either the disulfonic acids were sulfonated to trisulfonic acids or hydrolysis took place with formation of monosulfonic acids, the analytical procedure was also very inadequate, as the author admits.

Consequently, the literature does not report any general rule of transformation of isomeric naphthalene disulfonic acids, and we find only occasional and sometimes conflicting data about their isomerization. In these circumstances, we were prompted to undertake a systematic investigation of the isomerization of naphthalene disulfonic acids.

Isomerization of Naphthalene Disulfonic Acids at 100°

1,5-, 1,6- and 1,7-disulfonic acids were subjected to isomerization in 93.5% sulfuric acid at 100°. Results of experiments on the isomerization of the 1,5-acid are set forth in Table 1; these show that at the start the 1,6-isomer is preferentially formed, but later considerable amounts of 1,3- and 1,7-isomers are formed. The increasing

quantities of 1,3- and 1,7-isomers are evidently associated with secondary isomerization of the 1,6-acid which is less stable to hydrolysis than any of the other α,β-isomers. None of the sulfonic acid mixtures was found to contain 2,6- and 2,7- isomers. The content of 1,5-disulfonic acid, determined as xylidine, was higher than that determined as benzidine. The presence in the mixture of the 2,6-acid would have led to the reverse result since its xylidine salt is readily soluble [9].

TABLE 1

Isomerization of Naphthalene-1,5-disulfonic Acid in 93.5% Sulfuric Acid at 100-102°.

No. of expt.	Moles sulfuric acid per mole of disulfonic acid	Duration of heating (hrs.)	Comp. of mixture (% of total sulfonic acids)			
			1,5-acid		1,6-acid	1,3- and 1,7-acids
			As xylidine	As benzidine		
295	3.55	10	93.8	92.4	6.9	0
296	3.64	25	81.2	79.8	9.9	9.6
297	3.47	75	51.9	51.5		
298	6.93	10	91.7	91.0	8.7	0
299	7.01	25	64.9	63.6	22.2	13.6
300	6.99	75	14.8	13.4	45.1	40.8

With progressive reduction in the quantity of 1,5-isomer, the process correspondingly proceeds ever more in the direction of formation of the stable 2,6- and 2,7-isomers and of decrease of the amounts of 1,6-isomer and later of 1,3- and 1,7-isomers.

Consequently, the logical sequel to the isomerization of the 1,5-disulfonic acid is isomerization to the analogous 1,6- and 1,7-acids, results of experiments with which are set forth in Table 2.

TABLE 2

Isomerization of Naphthalene-1,6- and -1,7-disulfonic Acids in Presence of 7 Moles 93.5% Sulfuric Acid at 100-102°

No. of expt.	Isomerization of	Duration of heating (hrs.)	Comp. of mixture (in % of sum of disulfonic acids)				Ratio of 2,7- to 2,6-isomer
			2,6-	2,7-	1,6-	1,3- and 1,7	
302	1,6-	25	1.6	13.6	64.4	20.4	8.5
303	1,6-	75	2.5	23.5	48.4	25.5	9.4
316	1,6-	150	5.5	44.4	24.5	25.6	8.4
317	1,6-	300	7.9	58.1	13.6	20.4	7.4
328	1,6-	760	8.7	75.0	3.8	12.5	8.6
329	1,6-	1200	9.4	77.3	2.3	11.0	8.2
304	1,7-	25	1.8	15.1			8.4
306	1,7-	75	2.1	17.3	39.1	41.5	8.2

In the isomerization of the 1,6-acid it was actually found that the fall in amount of starting substance is accompanied by the appearance of 2,6- and 2,7-disulfonic acids which are not hydrolyzed in these conditions. For direct demonstration of the presence of the latter in the mixture, the disulfonic acids were isolated in the form of benzidine salts and transformed into chlorides which were identified by their melting points.

In all experiments the 2,6- and 2,7-isomers are formed in the approximate ratio of 1:8.5, as we had already noted previously in the sulfonation of the β-sulfonic acid. The data of Table 2 show that the amount of 1,3- and 1,7-isomers attains a maximum of about 26% and then falls off, but not as quickly as the amount of 1,6-isomer. With passage of time the sum of the 1,3- and 1,7-isomers ever more greatly exceeds the quantity of 1,6-acid due to the greater resistance to hydrolysis of the former.

The isomerization of the 1,7-isomer proceeds similarly to that of the 1,6-isomer.

Long-period experiments on isomerization of the 1,6-acid led to sulfonic acid mixtures containing a large amount of 2,7-isomer and a small amount of 2,6-isomer (experiment 328 and 329). Since at 100° all the isomers are hydrolyzed with appreciable speed, apart from the 2,6- and 2,7-isomers, isomerization proceeds irreversibly in the direction of formation of 2,6- and 2,7-isomers depending upon the conditions [1]. If the heating is prolonged much beyond the period of experiment 329, we can obtain a mixture consisting solely of 2,6- and 2,7-acids in the ratio of 1:8.5.

Isomerization of Disulfonic Acids at 130 and 140°

We attempted to accelerate the isomerization of the disulfonic acids by raising the temperature while retaining the initial ratio of 2,6- and 2,7-isomers. For this purpose we performed experiments at 130 and 140°.

The results of the experiments (Table 3) show that isomerization of the 1,5-acid proceeds so rapidly that after 10 hours the starting material could not be detected in the mixture with the help of m-xylidine. Isomerization of the formed 2,6- and 2,7-disulfonic acids was not observed at first, but later (when their amount rises) a change is noted in the original 1:8.5 ratio of the 2,6- to the 2,7-isomer in favor of the 2,6-acid which is the most stable isomer. Just as at 100°, mixtures are obtained with a high content of 2,7-isomer and a low content of 2,6-isomer (expt. 344 and 345).

TABLE 3
Isomerization of Naphthalene-1,5-disulfonic Acid in Presence of 3.5 Moles of 90% Sulfuric Acid at 130°

No. of Expt.	Duration of heating (hours)	Composition of mixture (in % of sum of disulfonic acids)				Ratio of 2,7- to 2,6-acids
		2,6-	2,7-	1,6-	1,3- and 1,7-	
343	10	2.5	20.8	50.6	26.1	8.3
344	25	6.8	55.9	18.1	19.2	8.2
345	35	8.8	66.3	11.3	13.6	7.5
349	50	16.5	61.5	11.8	10.2	3.7

At 130°, just as at 100°, the 1,5-acid gives predominantly the most labile of the α,β-isomers — the 1,6-isomer; subsequent enrichment takes place of the 1,3- and 1,7- and the more stable 2,6- and 2,7-isomers.

Isomerization of the disulfonic acids at 140° proceeds more rapidly than at 130°, which is reflected also in the rapid upsetting of the original ratios between the 2,6- and 2,7-isomers. Experiments were performed with three isomers. The results (Table 4) show that when the 1,5-acid is isomerized the total of 2,6-, 2,7- and 1,7- isomers is higher than when starting out from the 1,6-acid in identical conditions. This shows that in the former case the isomerization is more extensive, although it would appear that it should be reversible since the isomerization of the 1,5-acid is associated from the start with transition into α,β-isomers, whereas the 1,6-acid is already a α,β-isomer. This is explained by the ease of hydrolysis of the 1,5-acid to α-sulfonic acid and naphthalene, which rapidly leads to formation in the mass of β-naphthalenesulfonic acid; the latter is further sulfonated to α,β- and β,β-isomers; there is also rapid accumulation of α,β-isomers formed both by sulfonation of α- and of β-sulfonic acid. Consequently, the more labile is the isomer, the more rapidly and the more extensively does its isomerization proceed in the given conditions.

TABLE 4
Isomerization of Naphthalene Disulfonic Acid in Presence of 3 Moles of 87% Sulfuric Acid at 140°.

No. of Expt.	Isomer	Duration of heating (hours)	Composition of mixture (in % of sum of disulfonic acids)				Ratio of 2,7- to 2,6-acids
			2,6-	2,7-	1,6-	1,3- and 1,7-	
338	1,5	5	4.0	29.1	33.4	33.5	7.3
337	1,5	10	5.6	52.4	15.6	26.4	9.3
340	1,5	15	12.9	48.4			3.7
334	1,6	5	2.7	19.4	50.7	27.2	7.2
335	1,6	10	6.0	48.0	22.8	23.2	8.0
336	1,6	25	17.4	59.8	12.3	10.5	3.4
350	1,7	10	2.6	18.5	47.4	31.5	7.1

Isomerization of Disulfonic Acids at 160°

The 1,6-, 2,6- and 2,7-isomers were subjected to isomerization at 160°. The results of the experiments with the 1,6-acid (Table 5) show that isomerization is much more rapid than at 140°.

The original ratios of 2,6- and 2,7-isomers have already changed appreciably after 5 hours. The experiments also show that isomerization with 3 moles sulfuric acid proceeds more rapidly than with two moles. The same regularity was also observed in experiments with the 1,5-acid at 100° (Table 1). The results of the last three experiments of Table 5 show that the amount of 2,7-isomer rises to a maximum and then falls off while the quantity of 2,6-isomer continuously increases. Consequently, two experiments of this series must be regarded as a continuation of the experiments of the first series (with two moles sulfuric acid) in which the maximum for the amount of 2,7-isomer was not reached. In the experiments of Table 5 a state close to equilibrium between the isomers was not attained.

TABLE 5
Isomerization of Naphthalene-1,6-disulfonic Acid in Presence of 77% Sulfuric Acid at 159-160°.

No. of expt.	Moles sulfuric acid per mole sulfonic acid	Duration of heating (hrs.)	Composition of mixture (in % of sum of disulfonic acids)				Ratio of 2,7- and 2,6-isomers
			2,6-	2,7-	1,6-	1,3 and 1,7-	
330	2.02	2	2.2	20.7	44.8	32.3	9.4
331	2.02	5	13.2	37.4	30.1	19.3	2.7
332	2.03	10	19.0	50.7	17.7	12.6	2.7
333	2.03	25	25.4	57.1	8.9	8.1	2.2
325	3.00	5	15.7	49.5			3.1
326	3.09	10	23.8	59.5	8.6	8.1	2.5
327	3.17	25	28.3	55.7			2.0

In Table 6 are set forth the results of experiments with 2,6- and 2,7-disulfonic acids. These show that the process of isomerization of both isomers is considerably slower than the isomerization of the 1,6-isomer, while the 2,6-isomer, in turn, isomerizes more slowly than the 2,7-isomer. Also, in these cases, the labile isomer is rearranged more rapidly and more far-reachingly, as we already established above. No α,β-isomers were found in the mixture of experiment 307; it must be stated, however, that small amounts of them were present. The experiments showed that heating for 300 hours brings about a state close to equilibrium, since the composition of the sulfonic acid mixture is the same when starting either from the 2,6- or the 2,7-acid. A state close to equilibrium was also reached when starting from a mixture which had contained equal amounts of 2,6- and 2,7-isomers. The results of these experiments (Table 7) show that after heating for 300 hours, a mixture is obtained of the same composition as in the experiments of Table 6 (experiments 319, 321 and 322). Consequently, at 150°, the sulfonic acid mixture has the following composition in the equilibrium state (in %): 2,7-disulfonic acid 49; 2,6-disulfonic acid 31; 1,6-disulfonic acid 9; 1,3- and 1,7-disulfonic acids 11.

TABLE 6

Isomerization of Naphthalene-2,6- and -2,7-disulfonic Acids in Presence of 77% Sulfuric Acid at 158-160°

No. of expt.	Isomer	Moles sulfuric acid per mole sulfonic acid	Duration of heating (hrs.)	Composition of mixture as % of sum of disulfonic acids			
				2,6-	2,7-	1,6-	1,3- and 1,7-
307	2,6	2.01	10	92.5	7.5		
308	2,6	2.05	25	87.7	10.4		1.9
314	2,6	2.03	75	67.0	23.6	1.5	7.9
315	2,6	2.04	150	52.8	34.7	5.0	7.5
319	2,6	3.07	300	31.2	49.5	9.4	10.0
322	2,6	2.92	300	31.3	48.7	9.1	10.9
342	2,7	2.26	10	1.9	88.4		10.9
341	2,7	2.22	25	4.2	78.8	4.4	12.6
312	2,7	2.00	75	19.7	63.6	6.7	10.0
318	2,7	2.06	150	28.2	54.3	7.0	10.5
321	2,7	3.10	300	31.7	48.4	8.3	11.6

TABLE 7

Isomerization of Equal Parts 2,6- and 2,7-Acids in Presence of 3 Moles 77% Sulfuric Acid at 158-160°

No. of expt.	Duration of heating (hrs.)	Composition of mixture (as % of sum of disulfonic acids)			
		2,6-	2,7-	1,6-	1,3 and 1,7
323	150	28.7	52.9	7.5	10.9
324	300	31.2	49.3	6.1	13.4

During the formation of sulfonic acids, the labile isomers always make their appearance in preponderating amounts, but the subsequent processes of their hydrolysis and resulfonation change the original ratios in favor of the more stable isomers. This does not signify, however, that the quantity of the isomers in the equilibrium mixture (when all the isomers may be hydrolyzed) is determined only by the stability of the isomer; for in dynamic equilibrium the composition of a mixture is governed both by the velocity of hydrolysis and the velocity of formation of the given isomer.

Thus, the velocity of formation of the 2,7-isomer is 8.5 times that of the velocity of formation of the 2,6 isomer; in the equilibrium mixture, however, the ratio of 2,7- to 2,6-isomer is 1.58 due to the velocity of hydrolysis of the 2,7-isomer being greater than that of the 2,6-isomer.

Similar considerations apply to the ratios of 1,6-, 1,3- and 1,7-isomers. Although the 1,7- and 1,3- are more stable than the 1,6-isomer, the velocity of their formation is considerably lower, as we showed previously, hence the amount of each of them is less than the amount of 1,6-isomer.

All the isomeric disulfonic acids, apart from the 1,5-isomer, can originate from the β-sulfonic acid. At 160° the 1,5-isomer is present in the mixture in such small amounts that it cannot be detected. It is the most labile of all the isomers and hydrolyzes to the α-acid and naphthalene. The latter is rapidly sulfonated to a mixture consisting mainly of the more stable β-isomer and sulfonating far more quickly than the α-isomer. Consequently there is very little α-acid in the mixture to be sulfonated to the 1,5-acid, and moreover, it sulfonates less readily than the β-acid. The unfavorable conditions for formation of the 1,5-acid and its lability are the causes of its nearly complete absence from the sulfonic acid mixture at 160°.

EXPERIMENTAL

Experiments were run in the following manner: Into a test tube containing an accurately weighed amount of disulfonic acid (with a known content of water of crystallization) were weighed definite amounts of sulfuric acid and water. The test tube was sealed and heated with occasional shaking in an Eijkman apparatus. All the mixtures were homogeneous. The concentration of the sulfuric acid in the mixture was so chosen that at the given temperature it did not sulfonate the disulfonic acids to trisulfonic acids and did not lead to accumulation of monosulfonic

acids by hydrolysis. In all the experiments, the heating was followed by determination of the total acidity, since its constancy before and after heating demonstrated the absence of trisulfonation and of accumulation of monosulfonic acids. The experiments were performed in presence of 2-3 moles sulfuric acid (only at 100° was 7 moles sulfuric acid required for complete solution of the 1,5-disulfonic acid). The amounts of individual isomers were determined by our previously described methods [10]. Disulfonic acids were prepared by saponification in an aqueous-alcoholic medium of the disulfochlorides which were purified by crystallization until the melting points were those of the pure products.

SUMMARY

The process of isomerization of 1,5-, 1,6-, 1,7-, 2,6- and 2,7-disulfonic acids of naphthalene was studied at 100, 130, 140 and 160°. It was found that at 100°, the isomerization of the 1,5-, 1,6- and 1,7-disulfonic acids can proceed to the end in the direction of formation of 2,6- and 2,7-isomers which are formed in the ratio of 1:8.5.

At 160° a state close to equilibrium is reached with a content of 49% 2,7-acid, 31% 2,6-acid, 9% 1,6-acid and 11% 1,3- and 1,7-acids.

The relative amounts of isomers in the sulfonic acid mixture are governed by their resistance to hydrolysis and by the relative velocity of their formation. The more amenable an isomer to hydrolysis, the greater the speed of its formation.

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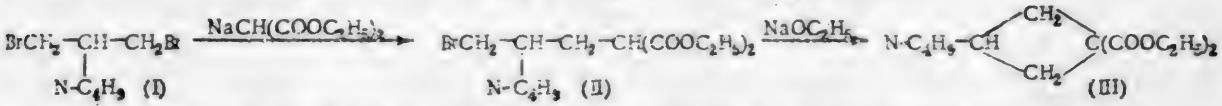
THE SELECTIVE MALONIC SYNTHESIS

III. THE ACTION OF SODIO-MALONIC ESTER ON 1-BROMO-2-BROMOMETHYLHEXANE

V. P. Golmov and N. M. Afanasyev

In previous researches [1, 2] it was shown that in the action of sodio-malonic ester on 1,3-, 1,5-, or 1,6-dihalo derivatives of symmetrical structure, the intermediate product of reaction —haloalkylmalonic ester— may be obtained in a yield of 60-70% of the theoretical if a considerable excess of malonic ester and dihalo derivative is used in relation to the amount of sodium ethylate. When, however, sodio-malonic ester acted on 4-bromo-3-bromomethyl-2-methylbutane [3], the yield of γ-bromo-β-isopropyl-propylmalonic ester was only 18% of the theoretical. In addition, a 46% yield was obtained of 1-isopropylcyclobutane-3,3-dicarboxylic ester, which illustrated the great facility with which the intermediate product underwent cyclization. The great ease of cyclization of γ-bromo-β-isopropyl-propylmalonic ester in comparison with γ-bromopropylmalonic ester, however, only applies in the instant of formation, for in the isolated state it is transformed by the action of sodium alcoholate into 1-isopropylcyclobutane-3,3-dicarboxylic ester in the very same yield in which cyclobutane-1,1-dicarboxylic ester is formed from γ-bromopropylmalonic ester (70% of the theoretical).

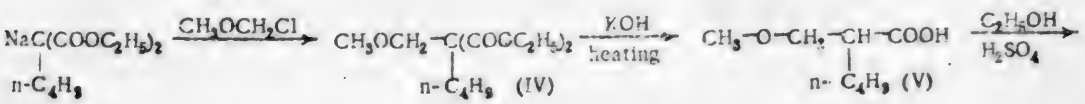
With the aim of establishing whether the yield of haloalkylmalonic ester is also influenced by other radicals located at the second carbon atom of 1,3-dihalo derivatives, we have now carried out the reaction between sodio-malonic ester and 1-bromo-2-bromomethylhexane (I) according to the following equation:

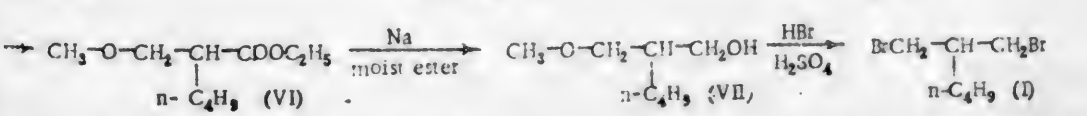


The investigation showed that the n-butyl radical in the molecule of the initial dibromo derivative has also a negative influence on the yield of intermediate product, although to a lesser degree than in the case of the isopropyl group. Thus, using four times as much as the calculated amount of malonic ester and twice as much dihalo derivative, we obtained γ-bromo-β-n-butylpropylmalonic ester (II) in a yield of 40.9% of the theoretical, together with 24.2% of the ester of 1-n-butylcyclobutane-3,3-dicarboxylic acid (III).

The action on isolated γ-bromo-β-n-butylpropylmalonic ester of sodium ethylate gave the ester of 1-n-butylcyclobutyl-3,3-dicarboxylic acid in a yield of 77.6% of the theoretical, i.e., little different from the yield with which other compounds containing a four-membered ring are formed in the same conditions from the respective γ-haloalkylmalonic esters [2, 4].

The 1-bromo-2-bromomethylhexane (not previously described in the literature) required for the research was synthesized by the method previously developed in the preparation of 4-bromo-3-bromomethyl-2-methylbutane:





This method evidently constitutes a general method for preparation of 1,3-dibromo derivatives of similar structure.

Saponification of methoxymethyl-n-butylmalonic ester followed by decarboxylation, as in the previous research [3], gives side by side with β-methoxy-α-n-butyl propionic acid [V] a fairly large amount of α-n-butylacrylic

acid. The analogous formation of α-ethylacrylic acid was recently observed by Zakharkin and Preobrazhensky [5] in the decarboxylation of ethoxymethyl-ethylmalonic acid.

EXPERIMENTAL

The starting substances for the investigation were n-butylmalonic ester (prepared by the action of n-butyl bromide on sodio-malonic ester [6]) and distilling at 97-98° at 5 mm) and the monochloromethyl ether with b.p. 55-60° [7].

Methoxymethyl-n-butylmalonic ester (IV). To 24.5 g (1 g-atom) pulverized metallic sodium, under a layer of 900 ml dry ether, was added as quickly as possible 324 g (1.5 mole) n-butylmalonic ester. After the whole of the sodium had dissolved, addition was made to the flask through a dropping funnel, with occasional shaking, of a solution of 150 g monochloromethyl ether in twice the volume of absolute ether. The reaction flask was cooled with water during the addition so that the reaction mixture did not come to the boil. After 24 hours, 800 ml water was added to the flask, the ethereal layer was separated, and the aqueous layer extracted once with ether. The combined ethereal solutions were dried with ignited calcium chloride, the ether was driven off and the residue was fractionated in vacuum. On the average, 18.6 g n-butyl malonic ester was obtained with b.p. 95-102° at 7 mm. and 316 g methoxymethyl-n-butylmalonic ester with b.p. 126-129° at 7 mm. Yield, allowing for the recovered n-butylmalonic ester, is 86.2% of the theoretical.

After a second vacuum distillation the product boiled at 115-116° (4 mm).

d_4^{26} 1.0014; n_D^{20} 1.4312; MR_D 67.13; calculated 67.19.

Found%: C 59.97; H 9.60. $C_{13}H_{24}O_5$. Calculated %: C 60.00; H 9.23.

By this method 1104 g methoxymethyl-n-butylmalonic ester was prepared.

Hydrolysis of methoxymethyl-n-butylmalonic ester. 220 g KOH was dissolved in 480 ml water and to the solution was added 400 ml 95% alcohol. The flask was then heated on an oil bath and to the hot alkali solution was added gradually 340 g methoxymethyl-n-butyl-malonic ester. The reaction mixture was boiled for 5 hours the alcohol was then distilled off and the cooled residue was extracted once with ether for removal of the unsaponified ester, of which 10 g was recovered.

Addition was then made to the liquid, with cooling, of the calculated amount of sulfuric acid diluted with twice the volume of water. The layer of acids was collected; the aqueous layer was extracted 3 times with ether; the ethereal extracts, combined with the main bulk of product, were dried with ignited calcium chloride and the ether driven off. The residue was decarboxylated by refluxing in an oil bath heated to 160-180°; after CO_2 had ceased to come off, the product was fractionated in vacuum.

Hydrolysis was carried out of 1100 g methoxymethyl-n-butylmalonic ester in this way and 110 g of a fraction with b.p. 94-95° (5 mm) and 440 g with b.p. 121-122° (5 mm) were obtained.

α-n-Butylacrylic acid. The 94-95° (5 mm) fraction was α-n-butylacrylic acid (yield 20.5% of the theoretical [8]).

d_4^{20} 0.9513; n_D^{20} 1.4426; MR_D 35.70; calculated 35.60.

Found %: C 65.48; H 9.58. $C_7H_{12}O_2$. Calculated %: C 65.62; H 9.37.

In ethereal solution the compound adds on one mole of bromine to form the bromide, a viscous oil. When kept in a sealed ampoule it polymerizes to a white, rubbery mass [8].

α-n-Butylacrylamide was prepared by the action of ammonia on the acid chloride, which, in turn, was prepared by the interaction of the acid with phsophorus pentachloride (b.p. of the acid chloride 165-168°). After recrystallization from carbon tetrachloride, α-n-butylacrylamide melted at 69°.

Found %: N 10.84. $C_7H_{13}ON$. Calculated %: N 11.02.

β-Methoxy-α-n-butylpropionic acid (V). The 121-122° (5 mm) fraction, resulting from hydrolysis of methoxymethyl n-butylmalonic ester, was β-methoxy-α-n-butyl propionic acid (yield 65% of the theoretical).

d_4^{26} 0.9766; n_D^{20} 1.4339; MR_D 42.56; calculated 42.32.

Found %: C 60.00; H 10.00. $C_8H_{16}O_3$. Calculated %: C 60.00; H 10.00.

Acid chloride of α-n-butylpropionic acid was prepared by the action of phosphorus pentachloride on the acid in the usual manner.

B.p. 175-177°; d_4^{20} 1.0129; n_D^{20} 1.4360; MR_D 46.08; calculated 46.03.

β-Methoxy-α-n-butylpropionamide was prepared by the action of ammonia on a solution of the acid chloride in ether. After recrystallization from ether it had m.p. 72°.

Found %: N 8.50. $C_8H_{17}O_2N$. Calculated %: N 8.80.

Ethyl ester of β-methoxy-α-n-butylpropionic acid (VI) was prepared in the following manner: 226 g β-methoxy-α-n-butylpropionic acid was heated on a water bath for 4 hours with 620 ml absolute alcohol and 62 ml concentrated H_2SO_4.

At the end of the reaction the product was poured into water, the layer of ester was collected; the aqueous layer was extracted with ether; the ether extract was added to the main bulk of product which was washed with water and dried with ignited calcium chloride; the ether was driven off and the residue distilled in vacuum. B.p. 78-79° at 4 mm. Yield 245 g, or 92.3% of the theoretical.

d_4^{20} 0.9186; n_D^{20} 1.4204; MR_D 51.73; calculated 51.57.

Found %: C 64.02; H 10.90. $C_{10}H_{20}O_3$. Calculated %: C 63.83; H 10.64.

β-Methoxy-α-n-butylpropyl alcohol (VII). Into a flask fitted with reflux condenser, dropping funnel, mechanical stirrer and thermometer reaching nearly to the bottom was run 140 ml saturated solution of sodium acetate, 200 ml ether and 63 g (0.33 mole) of the ester of β-methoxy-α-n-butylpropionic acid.

The flask was cooled with a mixture of ice and salt; with slow stirring and at −5 to −2°, 46 g (2 g-atoms) metallic sodium was added and simultaneously (dropwise) 30% acetic acid. The whole addition took about 8 hours. Water was then added until the separated salt had dissolved, the ether layer was separated, and the aqueous layer was extracted three times with ether. The combined ethereal solutions were dried with ignited potassium carbonate; the ether was then driven off, and the residue fractionated in vacuum when a fraction boiling at 91-92° (9 mm) was collected. In the flask remained a considerable amount of thick, dark oil. 418 g ester of β-methoxy-α-n-butylpropionic acid was reduced by the foregoing method to give 232 g β-methoxy-α-n-butylpropyl alcohol. Yield 71.4% of the theoretical.

d_4^{20} 0.8864, n_D^{20} 1.4320; MR_D 42.29; calculated 42.31.

Found %: C 65.79; H 12.10. $C_8H_{18}O_2$. Calculated %: C 65.75; H 12.33.

The p-nitrobenzoate, prepared in the usual manner by the action of p-nitrobenzoyl chloride on the alcohol, had m.p. 94-195° after recrystallization from aqueous alcohol.

1-Bromo-2-bromomethylhexane (I). Into a flask fitted with a reflux condenser were charged 514 g HBr (d = 1.50) and 96 ml sulfuric acid (d = 1.84). To this mixture was added 121 g (0.82 mole) β-methoxy-α-n-butylpropyl alcohol, and the whole was heated at the boil for 10 hours. The liquid darkened considerably during the process. At the conclusion of the heating, the reaction product was distilled off with steam; the lower layer of the distillate was separated, twice shaken with ½ of the volume of concentrated sulfuric acid, washed with sodium carbonate solution, dried with ignited $CaCl_2$ and distilled in vacuum. The sulfuric acid which had been used for washing the crude product was diluted with water and the layer formed (unreacted β-methoxy-α-n-butylpropyl alcohol) was distilled in vacuum when 15 g came over at 91-98°. (19 mm) 175 g pure 1-bromo-2-bromomethylhexane boiling at 102-103° (11 mm) was obtained. It was a colorless, heavy liquid with characteristic odor of dibromo compounds. Yield, allowing for recovered starting material, 61.3 % of the theoretical.

d_4^{20} 1.5254; n_D^{20} 1.5000, MR_D 50.40; calculated 50.06

Found %: C 32.60; H 5.49; Br 61.78 (Carius). $C_7H_{14}Br_2$. Calculated %: C 32.56; H 5.42; Br 62.14.

Action of sodio-malonic ester on 1-bromo-2-bromomethylhexane. To a solution of alcoholate prepared from 6.7 g (0.29 g-atom) metallic sodium and 100 ml absolute alcohol was added 186 g (1.16 mole) malonic ester followed by 150 g (0.58 mole) 1-bromo-2-bromomethylhexane. The reaction mixture was left at the normal temperature for 12 hours when a copious white precipitate of sodium bromide came down. The next day the mixture was heated on a bath for 4 hours, the reaction then becoming neutral. While cooling, 0.5 l. water was added, the layer of reaction products was separated; the aqueous layer was extracted with ether; the ethereal extracts were combined with the main bulk of reaction products, which were washed with water, dried with ignited calcium chloride and freed from ether; the residue was fractionated in vacuum

through a 20 cm Vigreux column.

Three fractionations gave 226 g of a fraction with b.p. 90-100° at 6 mm (mixture of malonic ester with original dibromo compound), 9 g of a fraction with b.p. 125-130° (1-n-butylcyclobutane-3,3-dicarboxylic ester (III), yield 24.2% of the theoretical), 40 g fraction with b.p. 155-165° (γ-bromo-β-n-butyl-propylmalonic ester (II), yield 40.9% of the theoretical) and 23 g residue. A second distillation of the 125-130° fraction gave b.p. 122-123° (5 mm).

d_4^{20} 1.0024; n_D^{20} 1.4397; MR_D 68.26; calculated 68.36.

Found %: C 65.39; H 9.12. $C_{14}H_{24}O_4$. Calculated %: C 65.62; H 9.37.

After distillation, the 155-165° fraction boiled at 154-155° (4 mm).

d_4^{20} 1.1835; n_D^{20} 1.4603; MR_D 78.03; calculated 77.93.

Found %: C 49.88; H 7.54; Br 23.47 (Carius). $C_{14}H_{25}O_4Br$. Calculated %: C 49.85; H 7.42; Br 23.44.

With the aim of utilizing the recovered starting substances, an experiment was performed in the following manner: To the alcoholate prepared from 6.7 g Na and 100 ml absolute alcohol was added at first 47 g malonic ester (0.29 mole), followed by the 90-100° fraction obtained in the previous experiment. This experiment was repeated three more times; in the first experiment 18 g fraction with b.p. 125-130° at 6 mm and 26 g fraction with b.p. 155-165° were obtained; the second run gave 29 g of 125-130° fraction and 4 g of 155-165° fraction; the third experiment gave 7 g of 125-130° fraction.

In all the four experiments there were used 280 g malonic ester, of which 167 g was recovered unchanged (amount consumed was 113 g or 0.7 mole), 26.8 g (1.12 g-atom) Na and 150 g (0.68 mole) 1-bromo-2-bromomethylhexane. The complete set of experiments gave 65 g (0.25 mole or 43.1% of the theoretical) of the ester of 1-n-butylcyclobutanedicarboxylic acid 70 g (0.21 mole or 36.2% of the theoretical) γ-bromo-β-n-butylpropylmalonic ester, and 38 g distillation residues from which it was impossible to separate any individual substances.

Cyclization of γ-bromo-β-n-butyl-propylmalonic ester. 1.7 g (0.074 g-atom) Na was dissolved in 100 ml absolute alcohol and to the alcoholate solution was added (with cooling) 25 g (0.074 mole) γ-bromo-β-n-butyl-propylmalonic ester. After standing at the ordinary temperature for 14 hours, the mixture was heated on a bath at the boil for 2 hours and then poured into 500 ml faintly acidified water; the mass was extracted 3 times with ether; the ethereal extract was washed with water and dried with ignited $CaCl_2$; the ether was driven off and the residue distilled in vacuum. Two distillations in a 20 cm Vigreux column gave 13 g of the ester of 1-n-butyl-cyclo-butane-3,3-dicarboxylic acid (b.p. 123-125° at 6 mm), and 2 g of the original bromoester (b.p. 155-167° at 6 mm) was recovered. The yield of cyclic product, allowing for the recovered material, is 77.6% of the theoretical.

1-n-Butylcyclobutane-3,3-dicarboxylic acid. 8 g of the ester of 1-n-butylcyclobutane-3,3-dicarboxylic acid was saponified with 20% aqueous alcoholic solution of KOH; the alcohol was distilled off from the solution and the residue was acidified, while cooling, with dilute sulfuric acid solution and extracted several times with ether. The ethereal extract was dried with ignited $CaCl_2$ and the solvent was driven off to leave 6.5 g crystalline acid which, after recrystallization from benzene, melted at 125-126°. Yield 92% of the theoretical.

Found %: C 60.16; H 8.07. $C_{12}H_{20}O_4$. Calculated %: C 60.00; H 8.00.

SUMMARY

1. 1-Bromo-2-bromomethylhexane was synthesized.

2. Treatment of it with sodio-malonic ester (4 moles malonic ester, 2 moles dibromo compound and 1 g-atom sodium) gave: the ester of γ-bromo-β-n-butylpropylmalonic acid in a yield of 40.9% of the theoretical and the ester of 1-n-butylcyclobutane-3,3-dicarboxylic acid in a yield of 24.2% of the theoretical.

3. When sodium alcoholate acts on γ-bromo-β-n-butyl-propylmalonic ester, the latter is transformed into the diethyl ester of 1-n-butylcyclobutane-3,3-dicarboxylic acid in a yield of 77.6% of the theoretical.

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EXPERIMENTAL DETERMINATION OF THE HEIGHT OF THE POTENTIAL BARRIER IN THE HYDROGEN BONDS OF BENZOQUINHYDRONE

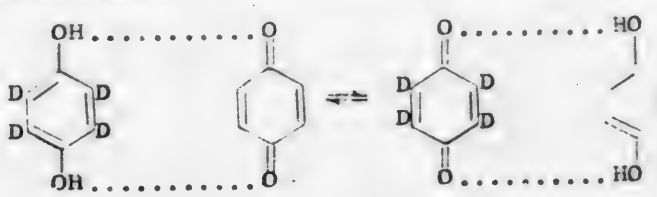
I. P. Gragerov and A. I. Brodsky

The problem of the position and mobility of the hydrogen atom in hydrogen bonds has not hitherto been closely studied. The potential curve of this atom may be represented as the sum of two intersecting curves forming two minima which are separated by a potential barrier. These minima correspond to two equilibrium positions, for example O−H . . . . . O and O . . . . . H−O and, especially at certain bond lengths, they can merge. The state of the hydrogen atom in hydrogen bonds is governed by the height of this potential barrier. If it is of a certain order of magnitude with zero vibration energy of the O−H (or alternatively of the X−H for the X−H . . . . . X bond), then the hydrogen atom very often moves from one position to another and hence is delocalized. At a high potential barrier the localization of this atom is maintained; such transitions as O−H . . . . . O⇌O . . . . . H−O are, however, possible (a type of tautomeric transformation), depending upon the height of the barrier which governs the energy of activation of this transformation. Finally, with a very high barrier the hydrogen atom is firmly fixed at one of the two atoms (or groups) linked by it.

The theoretical calculation of the height of the potential barrier in question for different hydrogen bonds has been carried out in a series of investigations with extremely conflicting results: from a few kcal/mole [1], for example 2, to 30 and more kcal/mole [2, 3, 4]. The majority of these calculations are based on questionable assumptions which deprive them of any quantitative reliability. This applies above all to the approximation of the potential curve of the X−H . . . . . X bond by the Morse function which is here invalid due to the great unharmonicity of the vibrations of the hydrogen bond itself [6]. For this reason the actual parameters selected for the calculation are very untrustworthy. This applies both to the identification of the frequencies, which has hitherto been a controversial point [7], and to the choice of bond lengths. Moreover, the calculated height of the barrier is greatly dependent on the given X−X distances, especially, on the equilibrium position of the hydrogen atom in the bond which, as we know, can still not be reliably measured. A change in the X−X distance by 0.2 A may change the calculated height of the barrier a hundredfold [2]. Furthermore, as was shown by M. I. Batuev [3], the height of the barrier is also highly dependent upon the nature of the end atoms or groups and differs completely from that of the isolated hydrogen bond to which, openly or indirectly, the majority of calculations relate. Finally, we have to remember that when the potential curve is asymmetric, the passage of hydrogen atoms through the barrier is accompanied by marked distortion of this curve due to rearrangement of the electron densities both inside the hydrogen bond and in other parts of the molecule.

We see from the foregoing data that the direct experimental determination of the height of the potential barrier in hydrogen bonds is a matter of considerable interest. Prior to the present investigation, it had never been undertaken. We made use of an isotopic method.

In previous researches one of us and G. F. Miklukhin [5] had shown that in benzoquinhydrone the hydrogen atoms of the hydrogen bonds remain near the hydroquinone nucleus so that the frequently propounded theory of oscillation of the hydrogen atom between two equilibrium positions or the theory of its delocalization is refuted by direct experiment in this case. Since up to now these researches were the sole direct experimental investigation of the problem under consideration, the question still remains open as to whether localization is a specific feature of the hydrogen bonds of benzoquinhydrone or whether it bears a general character. The observed localization of the hydrogen atom in hydrogen bonds points to a considerable height of the potential barrier between two minima corresponding to the two equilibrium positions of the hydrogen atom. This barrier (with accuracy down to zero energy) is equal to the energy of activation of the transformation:



(1)

which may be observed if one of the nuclei of the benzoquinhydrone molecule is labeled with deuterium, as was done in the cited investigations and as is indicated in the equation above.

In the previous investigations the possibility of slow transformation (equation 1) with a high activation energy was suggested. This is confirmed by the data below.

EXPERIMENTAL

The kinetics of reaction (1) may be studied with the help of deuterium because in the course of the reaction the nucleus of heavy hydroquinone is transformed into the nucleus of heavy quinone, while the nucleus of light quinone transformed into the nucleus of light hydroquinone. Consequently fractionation of the reaction product gives quinone containing heavy quinone in an amount which serves as a measure of the course of the reaction.

The benzoquinhydrone from heavy hydroquinone and ordinary quinone [5] were heated in quartz ampoules for a definite time at a given temperature and then separated into quinone and hydroquinone by fractional sublimation in high vacuum at 95°. Fractionation was complete after 45 minues, but after the first 15 minutes about 70% of the substance had been fractionated. The procedure differed from that previously described in that the operation was performed in a quartz vessel with small plugs of cotton wool. This change was dictated by the fact that glass catalyzes the reaction and was responsible for the poor reproducibility of our previous experiments.

In blank experiments with previously unheated quinhydrone, it was found that during the actual sublimation there is slow transfer of deuterium into the quinone, equal in our experimental conditions to 1.8%; the process shows good reproducibility when using identical amounts of material (0.3 g) and when the sublimation conditions are unchanged, as was the case in our investigation (see the first two experiments in Table 1). This correction is reduced in experiments with previously heated quinhydrone in accordance with transformation (1) which continued right up to the fractional sublimation. It is proportional to the degree of transformation before sublimation and it amounted in different experiments to 1.4 to 0.6% D.

Isotopic analysis was performed by the previously described procedure except that a microflotation method was applied which ensured an accuracy of 5% of the determined value and permitted the analysis of 0.04 - 0.05 g water. The initial content of deuterium in the hydroquinone nucleus was 25%.

In Table 1 are set forth the results of kinetic experiments. In addition to the observed percentage passage of deuterium into quinone x_1, the table gives the magnitude of x corrected for the transfer of deuterium during sublimation. The latter served as the basis of further kinetic calculations. As a check, the content of deuterium was determined also in the hydroquinone after fractionation. From the same table we see that both analyses in all cases are in sufficiently good agreement with each other.

TABLE 1

Duration of heating (min.)	Temp. (in °C)	Found % D in quinone (x_1)	Found % D in hydroquinone	Found % D sum	Corrected value of x	$-\ln(1-x/x_\infty)$
0	–	1.8	103	104.8	–	–
0	–	1.8	104	105.8	–	–
109	107.6	6.7	91	97.7	5.3	0.1122
109•		5.6	94.8	100.4	4.1	0.0856
220		10.5	92	102.5	9.4	0.2080
248•		8.2	93.5	101.7	6.9	0.1486
38•	115.1	9.4	93.5	102.9	8.2	0.1792
38		7.3	–	–	6.0	0.1280
80		11.9	92	103.9	10.9	0.2458
82		11.6	–	–	10.6	0.2383
120		15.5	90	105.5	14.8	0.3510
164		15.1	85.4	100.5	14.4	0.3397
164•		17.3	85.8	103.1	16.6	0.4040
20•	118.8	8.5	92	100.5	7.2	0.1548
20		10.0	–	–	8.9	0.1960
58•		15.3	89.1	104.4	14.6	0.3455
58		15.5	89.3	104.8	14.8	0.3510
115		18.0	85.3	103.3	17.4	0.4278
1254						

TREATMENT OF RESULTS

Transformation (1) corresponds to a reversible monomolecular reaction obeying the equation:

$$-\ln(1 - x/x_\infty) = K_1, \quad (2)$$

where $K = K_1 + K_2$ – the sum of the velocity constants of the forward and reverse reactions and x_∞ is the limiting equilibrium value of the magnitude x. Since the replacement of hydrogen by deuterium in the benzene ring cannot

• Heating was performed in nitrogen-filled ampoules. Note. Duration of sublimation 45 minutes.

substantially influence the energetic and kinetic properties of the investigated system,• then $K_1 = K_2$ and $x_{\infty} = 0.5$.

The dependence of the magnitude of $-\ln(1 - x/x_{\infty})$ on the duration is represented by the experimental points in Fig. 1. We see from this that approximately up to $x = 0.1$, the kinetics of the process satisfactorily accord with equation (2). With more prolonged heating the transfer slows down and the deviation from the equation of the monomolecular action constantly increases. These deviations must be attributed to some secondary reaction whose nature we could not establish. Evidently, connected with this anomaly is another one which was observed in lengthier experiments whose results are set forth in Table 2. We see from this table that not once could values of x exceeding 0.3 be reached.

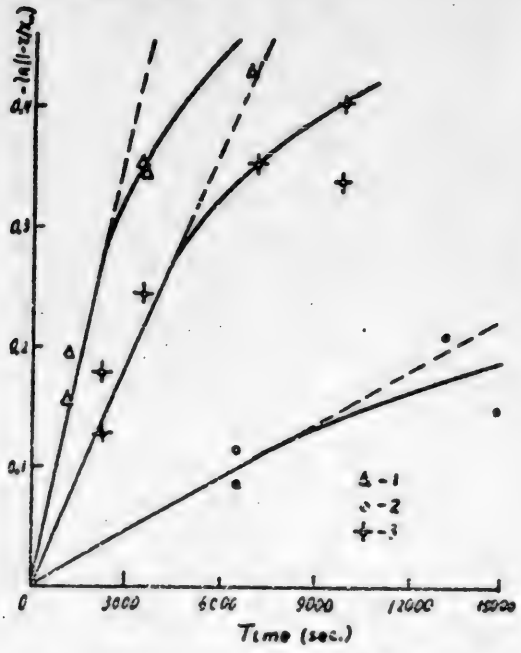


Fig. 1. Dependence of the velocity of transfer of deuterium from hydroquinone to quinone on the temperature. 1 - experiments at 119.8°; 2 - experiments at 107.6°; 3 - experiments at 115.1°

TABLE 2

Duration of heating (min.)	Temp. (in °C)	Found % D		
		in quinone	in hydroquinone	sum
60••	120°	27.4	74	101.4
1740••	120	26.5	73	99.5
180••	129-130	27.3	69	96.3
480••	129-130	26.8	71	97.8
2450•••	120	26.9	75.8	101.8
1800•••	115	20.6	77.2	97.8
2450••••	120	—	29.9	—
1800••••	115	85	17	102

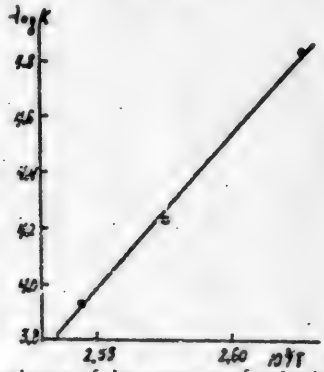


Fig. 2. Dependence of the constant of velocity of transfer of deuterium from hydroquinone to quinone on the temperature.

The further treatment of the experimental data was based on the fields in which these anomalies do not yet take effect, and in accordance with this we adopted for x_{∞} the value of 0.5••••• indicated above. The analytically interpolated straight lines of Fig. 1, give the following velocity constants K in sec.$^{-1}$:

Temperature	107.6	115.1	119.8°
K	$0.89 \cdot 10^{-3}$	$3.60 \cdot 10^{-3}$	$7.08 \cdot 10^{-3}$.

The scatter of the experimental points introduces a certain arbitrariness into the choice of slope of the straight lines, but we can readily convince ourselves that the different methods of interpolation, compatible with the experimental data, do not change the value of the activation energy by more than a few percent. We see from Fig. 2 that the values of $\log K = f(1/T)$ fall fairly consistently on a straight line for which we obtained (by the method of least squares):

$$\log K = 24.070 - 11.00 \cdot 10^3 \, 1/T. \qquad (3)$$

Application of the usual equation with a Boltzmann distribution of energy from two quadratic terms would give, according to (3)

$$K = 1.18 \cdot 10^{24} \cdot e^{-50314/RT}.$$

• This is confirmed by the data of the preceding research [5] and by the data in Table 2.

•• Heating in glass. ••• Heating in quartz. •••• Quinhydrone from ordinary hydroquinone in heavy quinone.

••••• Repetition of the calculation with $x_{\infty} = 0.25$ does not seriously influence the result: the velocity constants are reduced by a factor of 2, while the activation energy increases by less than 2 kcal/mole.

However, the value of 50.3 kcal/mole calculated by this method for the activation energy does not correspond to the actual value due to the application of the simplified energy distribution formula with two quadratic terms for the monomolecular decomposition reaction of such a complex molecule as quinhydrone in which the energy is distributed along many vibrating degrees of freedom. A sufficiently close approximation in such cases is obtained with the equation:

$$K = A\frac{(E/RT)^{m-1}}{(m-1)!}e^{-E/RT} = P \cdot e^{-E/RT} \qquad (4)$$

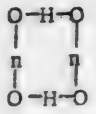
where P is a fore-exponential factor, E is the activation energy and m is the number of vibrating degrees of freedom of the activation energy. It has already been successfully used for the kinetics of a series of monomolecular reactions [8]. For its three parameters we have only two variables: the velocity constant and its temperature coefficient. The relation between the activation energy and the number of degrees of freedom may be directly obtained by comparison of the derivatives for 1/T from (3) and (4).

$$E/RT^2 - \frac{m-1}{T} = 11.00 \cdot 10^3 \cdot 2.3026,$$

from which, for a mean value of T = 387°, we find*

$$E = 30314 + 768.6\,(m-1). \qquad (5)$$

For unequivocal determination of the value of the activation energy, the number of degrees of freedom m must be given in addition.** It is plausible to assume that in the benzoquinhydrone molecule the internal vibrations of the nuclei (n) interact weakly with the vibrations of the atoms participiating in the formation of hydrogen bonds. This molecule must then be regarded as a system of 8 vibrating centers:



having m = 8·3 − 6 = 18 degrees of freedom. According to (5) we get E = 63380.

The value found for the activation energy, corresponding to the choice of the number of m, can be regarded as close to the upper limit of the actual value. With a smaller number of degrees of freedom, the latter may be lower by several kcal/mole. The scatter of the experimental points and other sources of error do not introduce an inaccuracy which should exceed the indicated magnitude.

Having substituted in (4) the magnitude log K = −4.354, calculated from (3) for the indicated mean temperature, we find log P = 24.11 + 0.434 (m − 1) or 31.49 for m = 18; hence:

$$K = 3.17 \cdot 10^{13} \frac{(63380/RT)^{17}}{17!} e^{-63380/RT}$$

This equation gives values for K which differ from the experimental ones by not more than 15%.

The high value of the fore-exponential factor, equal to $3 \cdot 10^{31}$ sec^{-1} may depend both on the fact that — in contrast to gaseous reactions — in the crystalline lattice the activation is effected by a transfer of vibratory energy, and on a possible chain mechanism of the propagation of process (1) in this lattice.

The comparatively high value of the activation energy (in round figures 63 kcal/mole) is easily accounted for by the reaction requiring the transfer of an atom of hydrogen in two hydrogen bonds with simultaneous far-reaching rearrangement of the remaining bonds. There is every reason to believe that both transitions take place in a single elementary act (in the kinetic sense). This is in accord with the inability (up to now) to detect the decomposition of benzoquinhydrone to the correspondence semiquinones [9]***.

* The dependence of log K on 1/T, according to (4), does not appreciably depart from linearity in the considered temperature range.

** For gaseous reactions it is usual to put the magnitude of A as that pressure below which a monomolecular reaction degenerates into a second order reaction [8]. This gives, in principle, the supplementary condition determining the value of m. Such a procedure is evidently here not applicable and its reliability is generally doubtful.

*** Decomposition to semiquinones should also have been manifested in the cited previous investigations and should have caused a more or less far-reaching delocalization of the hydrogen atoms.

Consequently, the height of the potential barrier of the hydrogen bond in benzoquinhydrone is equal to half of the activation energy, i.e. about 32 kcal/mole from the zero level of the valence vibration of OH or about 37 kcal/mole from the bottom of the potential trough of this bond.

For the reasons indicated above, a comparison of the values that we found with the theoretically calculated values do not present great interest, especially since the latter relate to other hydrogen atoms. Attention may be drawn, however, to two recent researchers, M.I. Batuev [3] calculated that the potential barrier of the OHO bond changes from 33.4 kcal/mole for water and 24 kcal/mole for propionic and higher saturated acids to 4.8 kcal/mole for crystalline β-oxalic acid. This author notes that his results agree with the localization of hydrogen bonds in benzoquinhydrone found in a previous investigation [5]. M. A. Kovner and V. A. Chuenkov [4] replaced for Morse function by another one which gave a rounded peak of the potential barrier, lowering its value by 8 kcal/mole. For formic, acetic and isovaleric acids they obtained 22-26 kcal/mole for one interpretation of the spectral frequencies and considerably lower values of 14-16 kcal/mole for other interpretations. They regard the last values as the more probable. We see from these data how strongly the calculated results are influenced by the identification of the spectral frequencies of the hydrogen bonds; this identification still remains uncertain. For the case considered in this study, the uncertainty is aggravated by the lack of X-ray and spectrographic data for benzoquinhydrone and its components. Consequently, we refrain from theoretical calculations aiming at a comparison with the experimental value found in this investigation.

We thank a fellow-worker in our laboratory, G. P. Miklukhin, and Prof. V. A. Roiter for valuable advice.

SUMMARY

1. With the help of deuterium a study was made of the passage of hydrogen atoms from hydroquinone nucleus into the quinone nucleus in the hydrogen bonds of benzoquinhydrone.

2. The energy of activation found for this process was about 63 kcal/mole, which corresponds to a height of the potential barrier of 32 kcal/mole in these bonds, reckoned from the level of zero energy of the valence vibrations of OH.

3. This first experimentally determined value of the potential barrier of the hydrogen bond was compared with the theoretically calculated values which only give a qualitative result due to the uncertainty of the parameters on which they are based.

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STRUCTURE AND PROPERTIES OF CELLULOSE ESTERS. 49.

INVESTIGATION OF THE CONDITIONS OF PREPARATION AND OF THE PROPERTIES OF STABLE DERIVATIVES OF CELLULOSE XANTHIC ACID

L. Aleksandru and Z. Rogovin

The sodium salt of cellulose xanthic acid (cellulose xanthate), the most important intermediate product of the viscose fiber industry, is known to be extremely unstable toward various influences. Cellulose xanthate is rapidly decomposed by the action of inorganic and organic acids, of caustic alkali and even of water. Gradual decomposition of this cellulose ester also takes place in contact with carbon dioxide from the air. The low stability of cellulose xanthate has prompted the investigation of a series of problems associated with the chemical structure of this compound. The preparation of derivatives of cellulose xanthic acid with adequate stability toward the action of saponifying agents and elevated temperature would provide the possibility of embarking on a systematic examination of the chemical structure of cellulose xanthate and, in particular, of the nature of the distribution of the ester groups in not highly esterified cellulose xanthate in dependence on the esterification conditions.

Cellulose xanthate is the sodium salt of an acid ester of the thiolthioncarbonic acid and cellulose. We know that neutral esters are more stable as a rule to the action of saponifying agents than are acid esters. This fact was established also for some neutral esters of thiolthioncarbonic acid with low-molecular alcohols [1]. We therefore suggested that esters of cellulose xanthic acid (i. neutral esters of thiolthioncarbonic acid) and other derivatives of this acid will possess enhanced stability to the action of acids and alkalies. The literature contains only contradictory statements about the preparation of the esters and some other derivatives of cellulose xanthic acid [2, 3]. Several patents have also been published in this field [4]. No references to systematic investigations of the stability of these compounds toward saponifying agents appear in the literature. In this paper we present the results of our own investigations of this subject.

EXPERIMENTAL

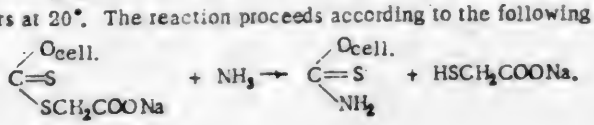
I. Preparation of derivatives of cellulose xanthic acid.

The materials that we selected for study of the stability of derivatives of cellulose xanthic acid toward acids, alkalies and heat were: cellulose xanthoacetic acid, cellulose xanthamide and cellulose methylxanthate.

1) Cellulose xanthoacetic acid was prepared by the action of sodium monochloroacetate on cellulose xanthate present in viscose solution neutralized with 3% acetic acid by the known procedure. When the aqueous solution of the sodium cellulose xanthoacetate is treated with 5% sulfuric acid, a white precipitate of cellulose xanthoacetic acid comes down.

The reaction was performed for 3 hours at 20°; the amount of monochloroacetic acid was 300% of the theoretical. In these conditions, starting from cellulose xanthate with $\gamma = 50$, we obtained a preparation of cellulose xanthoacetic acid with $k\gamma = 25$, which suggests that partial decomposition of the cellulose xanthate occurs in our chosen reaction conditions.

2) Cellulose xanthamide was prepared by reaction of sodium cellulose xanthoacetate in solution with 9 N ammonia solution for 24 hours at 20°. The reaction proceeds according to the following scheme:



A product was obtained with $\gamma = 25$.

3) The methyl ester of cellulose xanthic acid was prepared by two methods.

a) By conducting the methylation of cellulose xanthate in a heterogeneous medium. The starting material was pure cellulose xanthate. Dimethylsulfate was used as the methylating agent and anhydrous pyridine as the diluent. Following some preliminary experiments, it was established that the optimum conditions for preparation of the product were: duration 6 hours, temperature 20°, amount of dimethylsulfate 500% of the theoretical. In these conditions a product with $\gamma = 25$ was obtained.

b) By conducting the methylation of cellulose xanthate in a homogeneous medium; the reaction follows the same scheme.

When the reaction is performed in a weakly alkaline medium at 20° with 500% of the theoretical amount of dimethylsulfate, cellulose methylxanthate is obtained after only 5 minutes and there is no partial decomposition of the cellulose xanthate. Thus, for example, starting from cellulose xanthate with $\gamma = 50$, in these reactions a cellulose methylxanthate is obtained with the same degree of esterification. We also prepared cellulose methylxanthate with $\gamma = 75$ and $\gamma = 150$, starting from cellulose xanthate with the corresponding degree of esterification.

All our preparations of derivatives of cellulose xanthic acid, with $\gamma = 25$ to 50, are insoluble in caustic alkali and in other accessible solvents.

II. Investigation of the stability of derivatives of cellulose xanthic acid to the action of various reagents

1) Comparative investigation of the stability of derivatives of cellulose xanthic acid, cellulose xanthate, and cellulose acetate toward saponifying agents. It is a matter of great interest to compare the stability of the derivatives of cellulose xanthic acid that we prepared toward the action of saponifying agents (1 N solution of sulfuric acid and potassium hydroxide) as well as toward water at higher temperatures on the one hand with the stability of other industrially important cellulose esters on the other hand (in particular cellulose acetate, also cellulose xanthate). Our results are set forth in Table 1 and Figs. 1, 2 and 3.

TABLE 1*

Reagent used	Duration of treatment (in min.)	Amount of saponified ester groups (in % of original)				
		Cellulose xanthate	Cellulose xantho-acetate	Cellulose xanth-amide	Cellulose methyl xanthate	Cellulose acetate
1N H_2SO_4	15	After treatment	7.35	3.3	14	6.9
1N H_2SO_4	30	for 1-2 min. 100	20.6	12.6	32	15
1N H_2SO_4	60		74.2	51.5	80.2	39
1N NaOH	15	After treatment	16.8	15.9	18.1	12.8
1N NaOH	30	for 1-2 min. 100	74.8	38	80	27
1N NaOH	60		86	78	100	63
Water	60	93.8	3.3	1.1	7	0
Water	120	–	5.4	5.5	12	–
Water	240	–	–	15.4	23.6	–
Water	360	–	–	–	35.2	–

From the data of Table 1 and Figures 1, 2 and 3, we can draw the following conclusions: a) neutral esters of thiolthioncarbonic acid are many times more stable toward saponifying agents than acidic esters of the same acid; b) the stability of derivatives of cellulose xanthic acid changes in dependence on the character of the radicals entering into the composition of the molecule in their preparation. It must be noted, however, that even the least stable derivatives of cellulose xanthic acid are many times more stable than cellulose xanthate: c) all the derivatives of cellulose xanthic acid that we prepared are less stable toward saponifying agents than cellulose acetates, although the difference in stability of these cellulose esters is not very large.

2) Stability of derivatives of cellulose xanthic acid to heat (100°). The data obtained are set forth in Table 2.

It is seen from the data of Table 2, that cellulose xanthamide is more stable to high temperature than cellulose methylxanthate. The degree of esterification, however, of cellulose methylxanthate, also changes insignificantly when it is heated at 100° for 3 hours.

* All the investigations were carried out at 100°.

TABLE 2

Duration of heating (hrs.)	Amount of saponified ester groups (in % of original)	
	cellulose xanthamide	cellulose methylxanthate
3	0	5.1
6	0	13.65
12	2.2	32.1
18	27.5	59

3) Stability of derivatives of cellulose xanthic acid on prolonged storage and on exposure to bright light. Specimens of cellulose methylxanthate were kept at room temperature (20-30°) in a closed box without access to air. After storage for 90 days, the chemical composition of the cellulose methylxanthate had scarcely changed. The number of methyl groups had dropped from 3.52 to 3.19%. After the specimens of cellulose methylxanthate had been kept for 60 days with alternating exposure to moisture and bright light, partial saponification of the ester groups took place. In these conditions 19.83% of the total ester groups are saponified. This change is apparently due to oxidation processes since esters of xanthic acids, as well as xanthate, contain the >C=S group which is clearly unstable towards oxidizing action. We know, however, that ultraviolet rays bring about gradual saponification also of other cellulose esters, such as cellulose acetate and, especially, nitrocellulose.

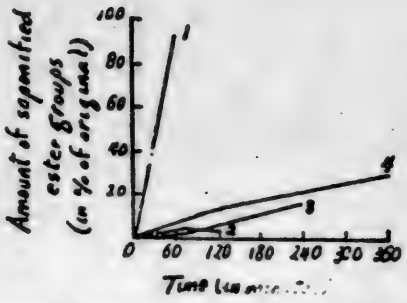


Fig. 3. Stability toward action of water at 100°. 1) Cellulose xanthate; 2) cellulose xanthoacetic acid; 3) cellulose xanthamide; 4) cellulose methylxanthate.

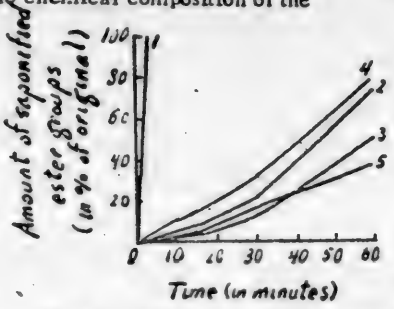


Fig. 1. Stability toward the action of 1 N sulfuric acid at 100°. 1) Cellulose xanthate; 2) cellulose xanthoacetic acid; 4) cellulose methylxanthate; 5) cellulose acetate.

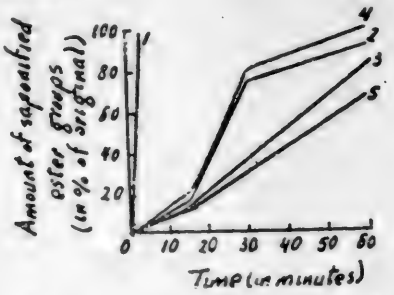


Fig. 2. Stability toward the action of 1 N NaOH at 100°. 1) Cellulose xanthate; 2) cellulose xanthoacetic acid; 3) cellulose xanthamide; 4) cellulose methylxanthate

SUMMARY

1. With the objective of establishing the possibility of preparing stable derivatives of cellulose xanthic acid, the following compounds were prepared and examined: a) cellulose xanthoacetic acid; b) cellulose xanthamide; c) cellulose methylxanthate.

2. It was shown that alkyl esters of cellulose xanthic acid (i.e., neutral esters of thiolthioncarbonic acid), as well as other derivatives of cellulose xanthic acid such as cellulose xanthoacetic acid and cellulose xanthamide, are considerably more resistant to the action of saponifying agents, to thermal action and to prolonged storage than acid salts of thiolthioncarbonic acid, and in particular than the sodium salt of cellulose xanthic acid.

The stability of esters of cellulose xanthic acid toward the foregoing treatments approximates that of other cellulose esters, for example cellulose acetate.

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STRUCTURE AND PROPERTIES OF CELLULOSE ESTERS. 50.

DISTRIBUTION OF THIOCARBONIC GROUPS BETWEEN PRIMARY AND SECONDARY ALCOHOLIC GROUPS IN CELLULOSE XANTHATE

L. Aleksandru and Z. Rogovin

Elucidation of the problem of the nature of the arrangement of thiocarbonic groups in the elementary chain of the cellulose xanthate macromolecule has great importance in the study of the chemical homogeneity of cellulose xanthate and of the effect of the esterification conditions on the properties of the resultant viscose solutions. Up to recently, the experimental study of this problem had met with difficulties due to the poor stability of the thiocarbonic group introduced into the cellulose macromolecule in the process of xanthation. After stable derivatives of cellulose xanthic acid had been prepared, the possibility arose of determining the position of the ester groups in not-fully-esterified cellulose xanthates. With this objective, we prepared a cellulose xanthate with $\gamma = 50$ by xanthation in normal conditions and also a cellulose xanthate with $\gamma = 100$ by supplementary esterification of cellulose xanthate in solution. In cellulose xanthate the position of the thiocarbonic groups is fixed by their methylation [1] which considerably increases the stability of these esters. We decided to prepare cellulose methylxanthate because in the preparation of this product, as we had shown [1], partial saponification of the thiocarbonic groups does not take place.

In cellulose methylxanthate the distribution was determined of the methylthiocarbonic groups between the primary and secondary alcoholic groups of the cellulose molecule. This investigation was performed with application of the method of tritylation of cellulose methylxanthate. As we know [2, 3], triphenylchloromethane selectively and completely esterifies the primary alcohol groups of cellulose in the 6-position with formation of the monotrityl ester of cellulose.

Preliminary experiments showed that the tritylation reaction (when performed without access of air) does not change the chemical composition of cellulose methylxanthate.

An attempt to utilize the method of treatment with iodic acid (which selectively and completely oxidizes the secondary alcoholic groups of cellulose in the 2- and 3-positions to aldehyde groups) for clarification of our problem did not meet with success. Treatment with iodic acid led to partial saponification of the methylthiocarbonic groups.

EXPERIMENTAL

1. Preparation of the mixed ester, cellulose tritylmethylxanthate. Cellulose methylxanthate was prepared by the previously described method [1]. Treatment of cellulose methylxanthate with triphenylchloromethane in presence of pyridine (which binds the evolved HCl) at 110° for 12 hours in absence of air gives the mixed ester, cellulose tritylmethylxanthate. We were the first to prepare this ester.

In our selected reaction conditions, the process of tritylation proceeds to the end. Increasing the esterification period to 20 hours did not change the content of trityl groups in the prepared mixed ester.

The mixed ester, cellulose tritylmethylxanthate, was obtained in the form of a dark-brown powder, difficultly soluble in pyridine. It is insoluble in other solvents. It decomposes at 127-129° with evolution of gases.

II. Determination of the ratio in the cellulose macromolecule of the primary and secondary alcohol groups esterified during the process of xanthation. During the investigation determinations were made of: a) the content of sulfur in cellulose xanthate used for preparation of cellulose methylxanthate; b) the content of sulfur and methyl groups in cellulose methylxanthate; c) the content of sulfur and trityl groups in the mixed ester, cellulose tritylmethylxanthate. Sulfur was determined by oxidation to sulfuric acid with a mixture of potassium permanganate and sodium carbonate [4]. Methyl groups were determined by the micro method of Viebock and Brecher [5]. The cellulose xanthate that we used contained 14.9% sulfur, i.e., the product had $\gamma = 50$. The cellulose methylxanthate contained 15.1% sulfur and 3.72% methyl groups, i.e., $\gamma = 50$.

Consequently, the thiocarbonic groups were not saponified in the preparation of cellulose methylxanthate. The fact that the content of sulfur and methyl groups corresponds to one and the same γ shows that all the methyl groups were linked through sulfur.

In the mixed ester, cellulose tritylmethylxanthate, the trityl groups were determined by saponification of the prepared mixed ester with sulfuric acid [6]. From the amount of sulfur present in this product, a determination was made of the total amount of methylthiocarbonic groups linked to the alcohol groups of cellulose in the mixed ester.

Since triphenylchloromethane selectively and completely esterifies the primary alcoholic groups of cellulose in the 6-position, the number of trityl groups is a measure of the number of substituted primary alcohol groups in the cellulose methylxanthate, and we can accordingly calculate from them the number of methylthiocarbonic groups linked in cellulose methylxanthate with the primary alcohol groups in the 6-position. From the difference between the total number of methylthiocarbonic groups in the investigated preparation and the number of these groups linked with the primary alcoholic group, we can determine the number of methylthiocarbonic groups linked with secondary alcoholic groups of the cellulose macromolecule in the 2- and 3-positions. The results are set forth in the table.

Starting product	Sulfur content				Content of trityl groups		No. of thiocarbonic groups (per 100 glucose residues)	
	in cellulose methylxanthate		in cellulose tritylmethylxanthate					
	in %	γ (for methylthiocarbonic groups)	in %	γ (for methylthiocarbonic groups)	in %	γ (for trityl groups)	at primary alcohol groups	at secondary alcohol groups
Cellulose	—	—	—	—	62.3	101	—	—
Cellulose xanthate with $\gamma = 50$	15.1	50	7.43	50	51.08	90	10	40
Cellulose xanthate with $\gamma = 100$	25.67	100	14.9	100	42.53	80	20	80

We see from the data in the table that the degree of esterification of cellulose methylxanthate does not change during the process of tritylation. The data show that during the xanthation reaction carried out as in normal technological conditions, as well as during supplementary xanthation in solution, 80% of the total number of thiocarbonic groups are linked with secondary alcohol groups in the 2- or 3-positions and only 20% of the thiocarbonic groups are linked with primary alcohol groups in the 6-positions.

In our opinion, this conclusion presents considerable interest because it clearly shows that in a number of cases the secondary alcohol groups of the cellulose macromolecule may be more reactive than primary alcohol groups during the esterification process.

It may be suggested that in the course of cellulose esterification reactions proceeding in an alkaline medium, the alcohol groups at the carbon atom in the 2-position (i.e., in the α-position to the carbon participating in the acetal bond and therefore possessing more acidic qualities) will be more reactive than the primary alcohol groups. This suggestion is confirmed by the results that we obtained when investigating the chemical structure of not-highly-esterified cellulose xanthates, as well as in some degree by the results recently obtained in the investigation of the structure of alkali cellulose [7].

SUMMARY

1. The mixed ester, cellulose tritylmethylxanthate, was prepared for the first time for the purpose of investigation of the distribution of thiocarbonic groups between the primary and secondary alcohol groups in the cellulose xanthate macromolecule.

2. The ratio between primary and secondary alcohol groups substituted during the xanthation of the cellulose macromolecule was determined.

3. It was shown that in the process of xanthation of cellulose both the primary and the secondary alcohol groups may react, but the secondary alcohol groups are the more reactive.

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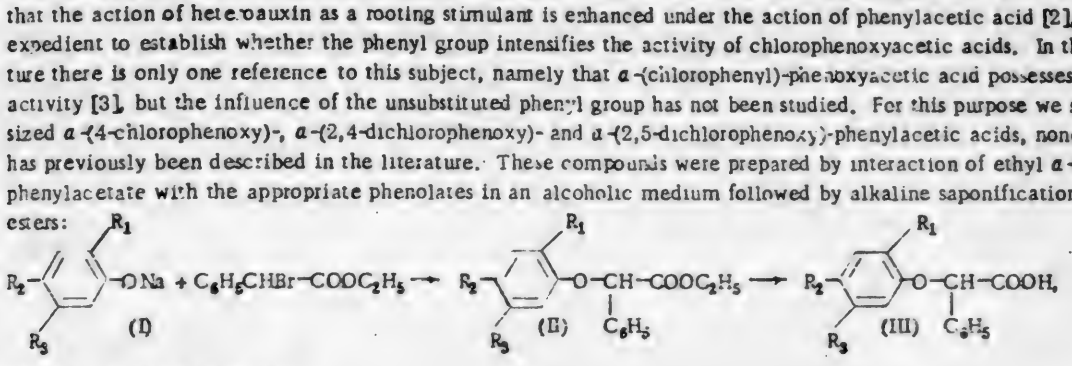
SYNTHESIS OF SOME CHLOROPHENOXY DERIVATIVES

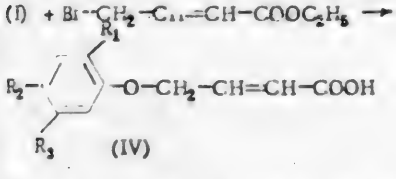
B. P. Mamaev, N. N. Suvorov and V. I. Gunar

A very large number of diverse substituted aryloxyalkane carboxylic acids have recently been synthesized and tested as plant growth promoters and herbicides. Much work in this field has been carried out in the Soviet Union by the late Academician S. S. Nametkin, N. N. Melnikov and their co-workers [1]. We may claim that the relation between physiological activity and chemical structure in this series has been very closely studied. However, some aspects of the subject have not been adequately clarified. One of these is the influence of the presence of a phenyl group in the α-position of ring-substituted phenoxyacetic acids on their activity. Since there is evidence that the action of heteroauxin as a rooting stimulant is enhanced under the action of phenylacetic acid [2], it was expedient to establish whether the phenyl group intensifies the activity of chlorophenoxyacetic acids. In the literature there is only one reference to this subject, namely that α-(chlorophenyl)-phenoxyacetic acid possesses a low activity [3], but the influence of the unsubstituted phenyl group has not been studied. For this purpose we synthesized α-(4-chlorophenoxy)-, α-(2,4-dichlorophenoxy)- and α-(2,5-dichlorophenoxy)-phenylacetic acids, none of which has previously been described in the literature. These compounds were prepared by interaction of ethyl α-bromophenylacetate with the appropriate phenolates in an alcoholic medium followed by alkaline saponification of the esters:



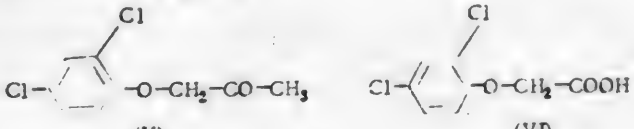
where R_1, R_2 and R_3 = H or Cl.

Specific interest also attaches to the problem of the activity of chlorophenoxycarboxylic acids containing a double bond in the side chain. In this connection it is interesting to note that α-naphthylvinylacetic acid is an active stimulator of root formation [4]. The chlorophenoxycrotonic acids required for settlement of this question were synthesized by condensation of γ-bromocrotonic acid esters with the appropriate phenolates followed by saponification of the resultant esters of γ-chlorophenoxycrotonic acids:



In this way we prepared γ-(4-chlorophenoxy)-, γ-(2,4-dichlorophenoxy)- and γ-(2,5-dichlorphenoxy)-crotonic acids.

Finally, taking into account the fact that in a number of cases the substitution of the hydroxyl group in the molecule of the physiologically active carboxylic acid by a methyl group, i.e., the transformation of the acid into the corresponding methylketone, leads to formation of an antagonist, we effected the synthesis of 2,4-dichlorophenoxyacetone (V), a possible antagonist of 2,4-dichlorophenoxyacetic acid (VI)



2,4-Dichlorophenoxyacetone was prepared by the reaction of potassium 2,4-dichlorophenate with bromoacetone.

Finally, it is our pleasant duty to extend our profound thanks to Academician V. M. Rodionov for his constant interest in this research.

EXPERIMENTAL

Ethyl α-bromophenylacetate was prepared by the procedure of V. M. Rodionov, N. N. Suvorov and K. S. Mikhailov [5]. 2,4-Dichlorophenol was prepared by direct chlorination of 2,5-dichloroaniline followed by replacement of diazo group by hydroxyl [7]. The ethyl and methyl esters of γ-bromocrotonic acid were prepared by bromination of the respective crotonic esters with N-bromosuccinimide [8].

Ethyl ester of α-(4-chlorophenoxy)-phenylacetic acid (II, $R_1=R_3=H$, $R_2=Cl$). To a solution of 6.17 g (0.11 mole) KOH in 60 ml absolute alcohol was added at first 12.9 g (0.1 mole) p-chlorophenol, and then 24.3 g (0.1 mole) ethyl α-bromophenylacetate. After standing for an hour at room temperature the reaction mixture was refluxed for 6 hours. The alcohol was then driven off, water was added to the residue until complete solution occurred of the KBr which had separated during the reaction, the oily layer was separated and the aqueous layer was twice extracted with ether. The ethereal extracts were combined with the main bulk of product and dried over anhydrous sodium sulfate. The ether was driven off and the residue was distilled in vacuum to give a fraction with b.p. 174-178° at 3 mm. Yield 19.1 g (66% of the theoretical). After a second distillation the substance crystallized on standing. M.p. 36-37°.

Found %: C 65.91, 65.98; H 5.36, 5.27. $C_{16}H_{15}O_3Cl$. Calculated %: C 66.10; H 5.16.

α-(4-Chlorophenoxy)-phenylacetic acid (III, $R_1=R_3=H$, $R_2=Cl$). 5 g (0.017 mole) ethyl ester of α-(4 chlorophenoxy)-phenylacetic acid is saponified by boiling with an alcoholic solution of 1.44 g (0.025 mole) KOH for 7 hours. The alcohol is driven off; the residue is dissolved in water and filtered; impurities are extracted with ether. The aqueous layer is acidified with hydrochloric acid (1:2). The precipitate is drained at the pump, washed with water and dried. Yield 4.2 g (61% of the theoretical). M.p. 160.5-161.5° (from toluene).

Found %: C 63.82, 63.79; H 4.37, 4.35. $C_{14}H_{11}O_3Cl$. Calculated %: C 64.00.

α-(2,4-Dichlorophenoxy)-phenylacetic acid (III, $R_1=R_3=H$, $R_2=Cl$). To a solution of sodium ethylate prepared from 0.95 g (0.04 g atom) sodium and 30 ml absolute alcohol was added 6.7 g (0.04 mole) 2,4-dichlorophenol and then 10 g (0.04 mole) ethyl α-bromophenylacetate. After standing for 30 minutes at room temperature, the mixture was refluxed for 6 hours. The alcohol was driven off, and the ethyl ester of α-(2,4-dichlorophenoxy)-phenylacetic acid was carefully extracted with ether. The ether was driven off and the residue saponified with a solution of 3.5 g KOH in 10 ml absolute alcohol (room temperature, 24 hours). The potassium salt of α-(2,4-dichlorophenoxy)-phenylacetic acid was dissolved in water and the solution made acid (to Congo) with hydrochloric acid. Yield 7.1 g (58.2% of the theoretical). M.P. 130.5-131.5°, rising to 134-134.5° after recrystallization from toluene.

Found %: C 56.93, 56.85; H 3.27, 3.43. $C_{14}H_{10}O_3Cl_2$. Calculated %: C 56.56; H 3.36.

Ethyl ester of α-(2,5-dichlorophenoxy)-phenylacetic acid (II, $R_1=R_3=Cl$, $R_2=H$). To a solution of sodium ethylate, prepared from 1.7 g (0.07 g-atom) sodium in 50 ml absolute alcohol, is added 12.18 g (0.07 mole) 2,5 dichlorophenol followed by 17 g (0.07 mole) ethyl α-bromophenylacetate. The reaction mixture is kept for an hour at room temperature and then boiled for 6 hours. The alcohol is driven off. The residue is extracted with absolute ether and the ether driven off, leaving a solid yellow residue. Recrystallization of the latter from methyl alcohol gives 16.62 g (73.2 % of the theoretical) ethyl ester of α-(2,5-dichlorophenoxy)-phenylacetic acid. M.p. 48°.

Found %: C 59.13, 58.99; H 4.44, 4.55. $C_{16}H_{14}O_3Cl_2$. Calculated %: C 59.10; H 4.34.

α-(2,5-Dichlorophenoxy)-phenylacetic acid. (III, $R_1=R_3=Cl$, $R_2=H$). 6 g (0.018 mole) ethyl ester of α-(2,5-dichlorophenoxy)-phenylacetic acid is saponified with a solution of 1.54 g (0.02 mole) KOH in a mixture of 6 ml alcohol and 15 ml water (refluxed for 6 hours). The reaction mixture is poured into 150 ml water and filtered; the filtrate is acidified (to Congo) with hydrochloric acid. The resultant precipitate is drained at the pump and twice crystallized from acetic acid. Yield 3.3 g (58% of the theoretical). M.p. 122-123°.

Found %: C 57.00, 57.15; H 3.53, 3.44. $C_{14}H_{10}O_3Cl_2$. Calculated %: C 56.56; H 3.36.

γ-(4-Chlorophenoxy)-crotonic acid. (IV, $R_1=R_3=H$, $R_2=Cl$). To a solution of sodium ethylate, prepared from 0.91 g (0.0395 g-atom) sodium and 15 ml absolute alcohol, is added a solution of 5.08 g (0.0395 mole) p-chlorophenol in 10 ml absolute alcohol, followed by 7.6 g (0.0395 mole) ethyl γ-bromocrotonate. After standing for 3 hours at room temperature, addition is made to the reaction mixture of a solution of 2.73 g (0.048 mole) KOH in 20 ml absolute alcohol. After 24 hours the mixture is poured into water, filtered and acidified with hydrochloric acid (to Congo). The residue is drained, washed and dried. Recrystallization from ligroin gives 3.85 g (46.4 % of the theoretical) of a substance with m.p. 96-97°.

Found %: C 56.66, 56.80; H 4.21, 4.38. $C_{16}H_9O_3Cl$. Calculated %: C 56.76; H 4.29

γ-(2,4-Dichlorophenoxy)-crotonic acid. (IV, R_1=R_2=Cl, R_3=H). To a solution of 2.8 g (0.05 mole) KOH in 30 ml absolute alcohol is added 8.1 g (0.05 mole) 2,4-dichlorophenol, followed by 8.75 g (0.05 mole) methyl γ-bromocrotonate. After standing at room temperature for 24 hours, the precipitated KBr is filtered off and to the filtrate is added a solution of 2.76 g (0.05 mole) KOH in 30 ml absolute alcohol; the mass is again stood at room temperature for 24 hours. The reaction mixture is poured into water and the impurities extracted with ether. The solution is acidified (to Congo) with hydrochloric acid (1:1), the precipitated acid is drained, dried and twice recrystallized from heptane. Yield 3 g γ-(2,4-dichlorophenoxy)-crotonic acid (24.5% of the theoretical) with m.p. 113-114°.

Found %: C 49.47, 49.26; H 3.47, 3.38. $C_{10}H_8O_3Cl_2$. Calculated %: C 48.58; H 3.25.

γ-(2,5-Dichlorophenoxy)-crotonic acid. (IV, R_1=R_2=Cl, R_2=H). To a solution of sodium ethylate, prepared from 0.67 g (0.029 g-atom) sodium and 15 ml absolute alcohol, is added, first, a solution of 4.8 g (0.029 mole) 2,5-dichlorophenol in 10 ml absolute alcohol, and then 6 g (0.03 mole) ethyl γ-bromocrotonate. After standing for 3 hours at room temperature, addition is made of a solution of 1.79 g (0.032 mole) KOH in 15 ml absolute alcohol, and the mixture is stood at room temperature for 24 hours. The mixture is then poured into 500 ml water, filtered, and acidified (to Congo). The acid, first precipitated in the form of an oil, rapidly crystallizes. It is drained, washed, dried and twice crystallized from heptane. Yield 4.34 g (63%). M.p. 99.5-100.5°.

Found %: C 49.21, 49.09; H 3.41, 3.26. $C_{10}H_8O_3Cl_2$. Calculated %: C 48.58, H 3.25.

2,4-Dichlorophenoxyacetone (V). To a solution of 2.8 g (0.05 mole) KOH in 25 ml methyl alcohol is added 8.2 g (0.05 mole) 2,4-dichlorophenol, followed by 4.7 ml (0.054 mole) bromoacetone. Heat is developed and KBr is precipitated. The reaction mixture is allowed to stand for 24 hours at room temperature; the precipitate is drained and washed with ether; the solvent is driven off from the filtrate. The residual oil is distilled in vacuum. Yield 6.75 g (61.5% of the theoretical). B.p. 140° at 4 mm. The distillate rapidly crystallizes. M.p. 53-54°. Crystallization from aqueous alcohol gives fine, colorless needles with m.p. 54-55°.

Found %: C 49.47, 49.65; H 3.80, 3.60. $C_9H_8O_2Cl_2$. Calculated %: C 49.45; H 3.65.

2,4-Dichlorophenoxyacetone semicarbazone, prepared by the usual method, forms colorless, fine crystals with m.p. 180-181°.

Found %: N 15.18, 15.01. $C_{10}H_{11}O_2N_3Cl_2$. Calculated %: N 15.21.

SUMMARY

The following were synthetized: α-(4-chlorophenoxy)-phenylacetic acid; α-(2,4-dichlorophenoxy)-phenylacetic acid; α-(2,5-dichlorophenoxy)-phenylacetic acid; γ-(4-chlorophenoxy)-crotonic acid; γ-(2,4-dichlorophenoxy)-crotonic acid; γ-(2,5-dichlorophenoxy)-crotonic acid; and 2,4-dichlorophenoxyacetone.

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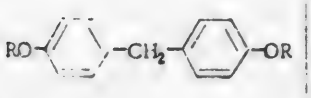
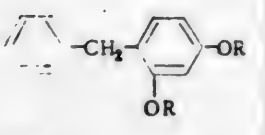
SYNTHESIS OF SUBSTITUTED HYDROXY- AND DIHYDROXYDIPHENYLMETHANES

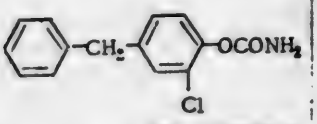
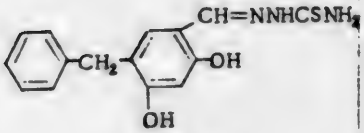
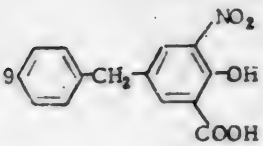
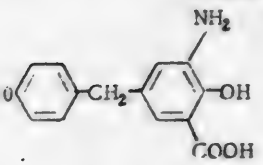
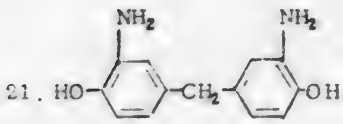
M. V. Rubtsov, E. E. Mikhlina and L. A. Pelenitsina

Diphenylmethane is known to possess bactericidal properties [1]. Taking into consideration the intensification of bactericidal action on introduction of hydroxyl or alkoxy groups, we synthesized a series of ethers of 4-hydroxydiphenylmethane, 4,4'-dihydroxydiphenylmethane and 2,4-dihydroxydiphenylmethane, also derivatives of diphenylmethane containing (in addition to hydroxyl groups) nitro, amino, formyl and carboxy groups. The prepared substances, their physical properties, results of analyses, and in vitro activity toward Trichophiton gypseum (trichophyton) and Mycobacterium tuberculosis (bacillus of human tuberculosis) are set forth in the table.

No.	Formula	Temperature		Empirical formula	Analytical results (in %)				Bacteriostatic activity in vitro, dilution 1:x	
		Of boiling	Of melting		Found		Calculated		bacillus of human tuberculosis x	trichophyton x
					C	H	C	H		
1	2	3	4	5	6	7	8	9	10	11
1	R = n-C_3H_7	177-179° (5 mm)	–	$C_{16}H_{18}O$	84.86	7.94	84.95	7.96	32,000	52,000
2	n-C_4H_9	184-186 (8 mm)	–	$C_{17}H_{20}O$	84.88	8.24	85.00	8.33	16,000	512,000
3	iso-C_5H_{11}	188-192 (11 mm)	–	$C_{18}H_{22}O$	85.03	8.31	85.04	8.66	512,000	512,000
4	CH_2—CH=CH_2	188-189 (15 mm)	–	$C_{16}H_{16}O$	85.53	6.97	85.76	7.14	512,000	512,000
5	n-C_6H_{13}	213-215 (13 mm)	–	$C_{19}H_{24}O$	85.26	8.98	85.07	8.95	4,000	1,000
6	n-C_8H_{17}	240 (19 mm)	30°	$C_{21}H_{28}O$	85.21	9.32	85.13	9.46	512,000	1,000
										
7	R = n-C_3H_7	220-222 (15 mm)	27	$C_{19}H_{24}O_2$	80.37	8.56	80.28	8.45	16,000	2,000
8	n-C_4H_9	223-224 (5 mm)	33	$C_{21}H_{28}O_2$	80.76	8.78	80.77	8.97	512,000	64,000
9	iso-C_5H_{11}	223-225 (3 mm)	36	$C_{23}H_{32}O_2$	81.25	9.22	81.18	9.41	1,638,000	1,024,000
10	n-C_8H_{17}	245 (5 mm)	45	$C_{28}H_{44}O_2$	82.12	10.30	82.07	10.37	256,000	0
										
11	R = CH_3	178 (7 mm)	–	$C_{15}H_{16}O_2$	78.60	7.08	78.95	7.02	≥512,000	64,000

(continued)

Table -- (continued)

1	2	3	4	5	6	7	8	9	10	11
12	R = C_2H_5	174-176 (4 mm)	–	$C_{17}H_{20}O_2$	79.54	8.06	79.67	7.81	1,638,000	1.124,000
13	n-C_3H_7	201-203 (5 mm)	–	$C_{18}H_{24}O_2$	80.16	8.58	80.28	8.45	>256,000	8,000
14	n-C_4H_9	205-208 (4 mm)	–	$C_{21}H_{28}O_2$	80.37	8.63	80.77	8.97	256,000	16,000
15	iso-C_5H_{11}	221-224 (7 mm)	–	$C_{23}H_{32}O_2$	81.23	9.18	81.18	9.41	>512,000	64,000
16	n-C_8H_{17}	235-240 (5 mm)	–	$C_{29}H_{46}O_2$	82.12	10.14	82.07	10.37	256,000	1,000
17		–	141-142°	$C_{14}H_{12}O_2NCl$	5.38	13.50 •••	5.35	13.57 •••	–	–
18		–	207-208	$C_{15}H_{15}O_2N_3S$		9.86 ••		10.63 ••	128,000	0
19		–	122-124	$C_{14}H_{11}O_5N$		5.22 •		5.13 •	128,000	4,000
20		–	209-210	$C_{14}H_{13}O_3N$		5.52		5.76 •	0	0
21		–	172-175	$C_{12}H_{14}O_2N_2$		11.80 •		12.17 •	32,000	2 000

According to the literature data, 4,4'-dihydroxydiphenylmethane is obtained together with 2,4'-dihydroxydiphenylmethane by interaction of phenol and formaldehyde in presence of dilute hydrochloric acid [2]. The total yield of the two isomers under various experimental conditions is 12-15%. Fractionation of the isomers is effected by distillation in vacuum followed by fractional crystallization from large amounts of water. We obtained a mixture of 4,4'- and 2,4'-dihydroxydiphenylmethanes by condensing two moles of phenol with one mole of formaldehyde in presence of dilute hydrochloric acid at room temperature. The isomers were separated by fractional precipitation of their methanol solution with water; in this way the over-all yield was raised to 21%. 2,4-Dihydroxydiphenylmethane was obtained, as described by Klarmann [3], by reaction of resorcinol with benzyl chloride in presence of aluminum chloride in nitrobenzene solution. Fractionation of the reaction products was effected by us by direct distillation in vacuum instead of by the laborious chemical treatment proposed by Klarmann.

Ethers of diphydroxydiphenylmethanes were synthesized by two methods: by heating molar amounts of the respective hydroxy- or dihydroxydiphenylmethane, alkyl halide and KOH in alcoholic solution; or by heating sodium benzylphenolates with the molecular equivalent of alkyl halide in toluene solution.

• Analytical results for nitrogen

•• Analytical results for sulfur

••• Analytical results for chlorine

For the synthesis of the carbamino ether of 3-chloro-4 hydroxydiphenylmethane (prep. No. 17), 4-hydroxydiphenylmethane was transformed with the help of sulfuryl chloride into 3-chloro 4-hydroxydiphenylmethane [4], successive reaction of which with carbonyl chloride and ammonia gave the corresponding carbamino ether [5]. Formylation of 2,4 dihydroxydiphenylmethane with formaniide [6] leads to 2,4-dihydroxy-5-formyldiphenylmethane, which by the usual procedure was transformed into the thiosemicarbazone (prep. no. 18).

According to the literature data, 3-carboxy-4-hydroxydiphenylmethane is formed by treating sodium benzylphenate with carbon dioxide [7]. We synthesized this compound by condensing benzyl chloride with methyl salicylate in presence of zinc chloride; the resultant 3-carbomethoxy-4 hydroxydiphenylmethane was saponified to 3-carboxy-4-hydroxydiphenylmethane. Nitration of the latter compound gave 3-carboxy-4-hydroxy-5-nitrodiphenylmethane (prep. No. 19), which was further subjected to reduction to 3-carboxy 4-hydroxy-5-aminodiphenylmethane (prep. No. 20).

Reduction of 3,3' dinitro-4,4'-dihydroxydiphenylmethane, synthesized by the patented procedure [8], gave 3,3'-diamino-4,4'-dihydroxydiphenylmethane (prep. No. 21).

The majority of the prepared compounds showed considerable activity in vitro toward Mycobacterium tuberculosis and Trichophiton gypseum. Negative results were obtained, however, in tests in vivo.

EXPERIMENTAL

4,4'- and 2,4'-dihydroxydiphenylmethane. A mixture of 200 g phenol, 86 g 37% aqueous formaldehyde, 317 ml concentrated HCl and 1270 ml water was mixed at room temperature for 48 hours. A frothy mass formed in the flask and consisted of a mixture of solid particles and oily drops. On filtration a large proportion of the oil goes into the filtrate and oily crystals remain on the filter. The latter are dissolved in cold methyl alcohol and water is added until turbidity appears. The crystals are drained at the pump and dried. M.p. 159-160°. Yield 25.6 g or 12% of the theoretical.

The filtrate after collection of the 4,4'-dihydroxydiphenylmethane is diluted with water until an oily layer is formed; this is separated and added to the main bulk of oil obtained from the mother liquor when filtering the reaction mass. The oily liquid is dissolved in ether, the ethereal solution is washed with water and dried with sodium sulfate. After removal of the ether, the residue is distilled in vacuum. Phenol first comes over and is followed by 2,4'-dihydroxydiphenylmethane. B.p. 204-208° at 6 mm. The substance quickly crystallizes. After recrystallization from water the m.p. is 114-116°. Yield 19.3 g or 9% of the theoretical.

Scheiber gives m.p. 160° for 4,4'-dihydroxydiphenylmethane and 115-116° for 2,4' dihydroxydiphenylmethane [2].

2,4-Dihydroxydiphenylmethane. To a cooled solution of 60 g resorcinol in 300 ml nitrobenzene is added a solution of 36 g benzyl chloride and 36 g aluminum chloride. The reaction mass is heated at 70° for 2 hours, cooled, and poured onto ice. The aqueous layer is separated from the nitrobenzene layer and extracted with ether; the ethereal extract is combined with the nitrobenzene solution which is washed with water, then with saturated sodium carbonate solution, and dried with sodium sulfate. The ether is driven off and the residue distilled in vacuum. Nitrobenzene first comes over, followed by unreacted resorcinol, and finally by 2,4-dihydroxydiphenylmethane in the form of a yellow, viscous liquid. After two distillations, the 2,4-dihydroxydiphenylmethane slowly crystallizes on standing. Crystallization is more easily effected by dissolving the distilled material in hot benzene and gradually cooling the benzene solution. Colorless crystals, m.p. 74-76°. Yield 25.4 g or 44.6% of the theoretical. The literature [3] reports a yield of 50%, m.p. 76°.

Propyl ether of 4-hydroxydiphenylmethane. To a solution of 1.54 g KOH in 20 ml absolute alcohol is added 5 g 4-hydroxydiphenylmethane and 3.34 g n-propyl bromide. The reaction mass is heated at the boil for 3 hours, then cooled and treated with 60 ml water. The oily layer is separated; the aqueous layer is extracted with ether; the ethereal extract is combined with the separated oil which is dried with sodium sulfate. The ether is driven off and the residue distilled in vacuum. Yield 5.24 g or 85.5% of the theoretical. Colorless liquid, readily soluble in organic solvents, insoluble in water.

Octyl ether of 4-hydroxydiphenylmethane. To an alcoholic solution of sodium ethylate, prepared from 0.88 g sodium and 18 ml absolute alcohol, is added 7 g 4-hydroxydiphenylmethane. The alcohol is distilled off in vacuum. To the solid sodium benzylphenate is added 24 ml dry toluene and 7.35 g n-octyl bromide. The mixture is heated at the boil for 8 hours. The cooled reaction mixture is treated with 50 ml water; the toluene layer is separated and dried with sodium sulfate. The toluene is driven off and the residue distilled in vacuum. On standing, the compound crystallizes. White crystalline powder, readily soluble in organic solvents, insoluble in water. Yield 7.83 g or 63.5% of the theoretical.

Carbamino ether of 3-chloro-4-hydroxydiphenylmethane. To a solution of 40 g carbonyl chloride in 230 ml dry benzene is added, with stirring and cooling, a solution of 58 g 3-chloro-4-hydroxydiphenylmethane [4] in a mixture of 30 ml benzene and 40 g dimethylaniline. The reaction mass is mixed for 3 hours at room temperature. Addition is then made of 10 ml conc. hydrochloric acid with good stirring. The benzene layer is collected and washed with water and slowly run into 80 ml 25% aqueous ammonia, cooled with ice. The reaction mass is kept for 15 hours at room temperature. The precipitated carbamino ether of 3-chloro-4-hydroxydiphenylmethane is filtered, washed with water and dried. After recrystallization from alcohol it has m.p. 141-142°. A white crystalline powder, readily soluble in alcohol, ether, acetone, insoluble in water. Yield 32 g or 37.5% of the theoretical.

2,4-Dihydroxy-5-formyldiphenylmethane. To a cooled solution of 4 g 2,4-dihydroxydiphenylmethane and 2.4 g formanilide in 20 ml absolute ether is added 1 g phosphorus oxychloride. The reaction mass is brought to the boil, gradually cooled and left at room temperature for 12 hours. Addition is then made of 100 ml 3% sodium hydroxide solution and the aniline is distilled off. The residue is acidified with 10% sulfuric acid and extracted with ether. The ethereal solution is dried with sodium sulfate. From the brown, viscous residue (after removal of the ether) a thiosemicarbazone is prepared by the usual method and has m.p. 207-208°. (After recrystallization from alcohol). Orange-yellow crystalline powder, readily soluble in acetone and alcohol, insoluble in water.

3-Carbomethoxy-4-hydroxydiphenylmethane. 12.7 g benzyl chloride, 30.4 g methyl salicylate and 2.5 g zinc chloride are heated to 65° at which temperature hydrogen chloride begins to come off violently. When the evolution of HCl has slowed down, the reaction mass is heated on a boiling water bath for 3 hours. The cooled reaction mass is poured into 100 ml water. The oily layer is collected and the aqueous layer extracted with ether; the ethereal extracts are added to the oil which is washed with water and dried with sodium sulfate. The ether is driven off and the residue distilled in vacuum. A fraction boiling between 170 and 190° at 3 mm is collected. It crystallizes on standing. After recrystallization from alcohol, 9.2 g 3-carbomethoxy-4-hydroxydiphenylmethane with m.p. 76-77° is obtained. White crystals, readily soluble in the common organic solvents, insoluble in water. Yield 38% of the theoretical.

3-Carboxy-4-hydroxydiphenylmethane. 5 g 3-carbomethoxy-4-hydroxydiphenylmethane and 15 ml 10% NaOH solution are heated at the boil for 2½ hours. The cooled reaction mass is treated with 17% hydrochloric acid until acid to Congo. The precipitated white crystals are drained at the pump, washed with water and dried. M.p. 139°. Yield 4.6 g or 98% of the theoretical. The literature [7] reports m.p. 139-140°.

3-Carboxy-4-hydroxy-5-nitrodiphenylmethane. To a solution of 5 g 3-carboxy-4-hydroxydiphenylmethane in 50 ml acetic acid is added 1 ml nitrous acid (s.g. 1.51) at 8-10°. The reaction mass is mixed for 3 hours and then poured into cold water. The precipitate is filtered, washed with water and dried in the air. Yellow crystalline powder, readily soluble in alcohol, insoluble in ether or water. M.p. 122-124° (from aqueous alcohol). Yield 5.1 g or 85% of the theoretical.

3-Carboxy-4-hydroxy-5-aminodiphenylmethane. A solution of 3 g 3-carboxy-4-hydroxy-5-nitrodiphenylmethane in 30 ml alcohol is reduced in presence of 3 g skeletal nickel catalyst at room temperature. At the conclusion of hydrogen absorption, the catalyst is filtered off, the alcoholic solution is evaporated to dryness in vacuum and the residue is recrystallized from aqueous alcohol. White powder, darkening in the air, readily soluble in alcohol, poorly soluble in water, ether and acetone. M.p. 209-210°. Yield 1.26 g or 47.2% of the theoretical.

3,3'-Diamino-4,4'-dihydroxydiphenylmethane. A solution of 10 g 3,3'-dinitro-4,4'-dihydroxydiphenylmethane in 200 ml alcohol is reduced in presence of 10 g skeletal nickel catalyst at room temperature. After absorption of the theoretical amount of hydrogen, the catalyst is filtered off and the alcoholic solution evaporated in vacuum. The product is purified by conversion to the hydrochloride and by regeneration with saturated sodium bicarbonate solution. A light-brown, crystalline powder, readily soluble in alcohol and acetone, poorly in ether, insoluble in water. M.p. 172-175°. Yield 6.25 g or 78.6% of the theoretical.

SUMMARY

1. The methods described in the literature for preparation of 4,4'- and 2,4'-dihydroxydiphenylmethanes have been simplified.

2. A series of new derivatives of hydroxy- and dihydroxydiphenylmethanes have been synthesized and tested for chemotherapeutic activity.

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SYNTHESIS OF HYDROCARBONS OF THE 1,2-BENZANTHRACENE SERIES

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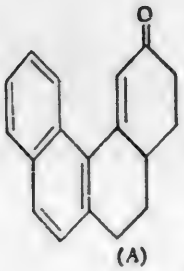
It was previously shown [1] that α-(3-chlorocrotyl)-γ-(2-naphthyl)-butyric acid undergoes intramolecular acylation in the 1-position when treated with sulfuric acid; this is followed by a second cyclization of the intermediate 1,5-diketone with formation of a tetracyclic ketone with the carbon skeleton of 3,4-benzophenanthrene (A).

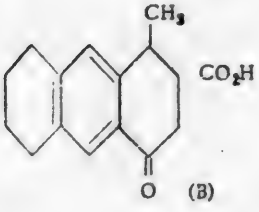


(A)

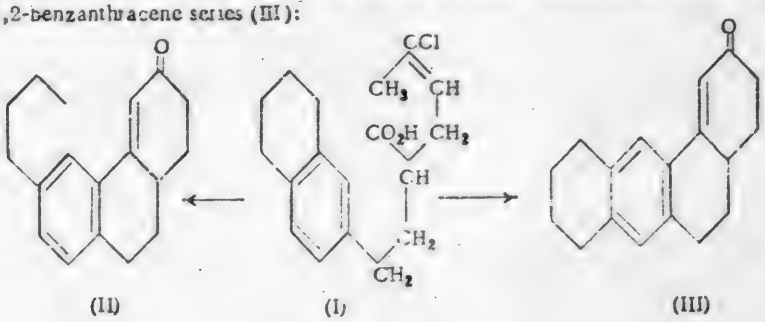
γ-(2-Naphthyl)-butyric acids which are alkylated in the side chain and in the naphthalene nucleus are also generally cyclized in the 1-position, but in exceptional cases the alkyl groups occupying certain positions in the nucleus (for example the 8-position) alter the direction of cyclization of naphthalenebutyric acids [2]. Saturation of one of the rings of the naphthalene nucleus brings about a similar effect; cyclization of γ-(5,6,7,8-tetrahydro-2-naphthyl)-butyryl chloride by heating under reduced pressure leads to a mixture of approximately equal parts of ketones of the phenanthrene and anthracene series [3].

On cyclization of the same acid with the help of conc. sulfuric acid, other authors [4] obtained a ketone of the anthracene series as the sole product. Similar observations were made in an attempt to prepare 1-methyl-2-carboxy-4-keto-octahydrophenanthrene [5]; contrary to the author's expectation, treatment of the initial anhydride of α-(5,6,7,8-tetrahydro-2-naphthyl)-ethylsuccinic acid with aluminum chloride in nitrobenzene led to its complete cyclization into the corresponding anthracene derivative (B). Consequently, in these cases tetralylbutyric acids, like the nuclear-substituted phenylbutyric acids, are acylated in the p-position with respect to the original substituent.

On the basis of the cited data, it was to be expected that sulfuric acid hydrolysis and cyclization of α-(3-chlorocrotyl)-γ-(5,6,7,8-tetrahydro-2-naphthyl)-butyric acid (I) would yield not the 3,4-benzophenanthrene derivative (II) but the isomeric compound of the 1,2-benzanthracene series (III):

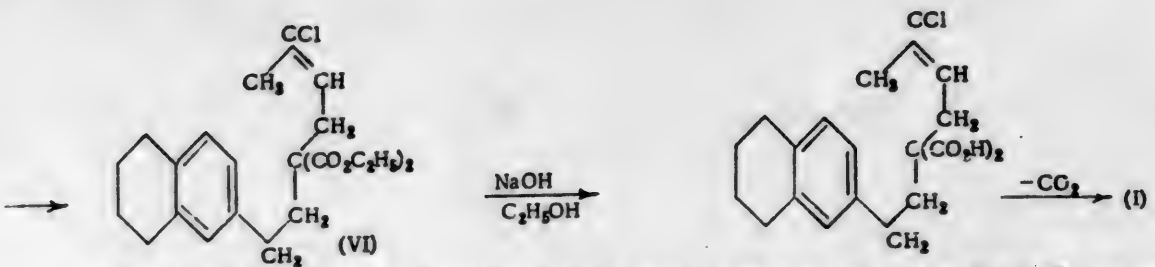


(B)



(II) (I) (III)

1,2-Benzanthracene and its homologs constitute, in respect their biological properties, a most interesting series of tetracyclic aromatic hydrocarbons with four condensed rings. At the present time several synthetic metho supplementing one another, are known and extensively employed for the synthesis of benzanthracene homologs: a large number of these have been developed by B. M. Mikhailov and co-workers [6]. Since the above scheme could prove convenient as a new route to hydrocarbons of the benzanthracene series, it was decided to attempt the synthesis of acid (I) and to study the product of its sulfuric acid hydrolysis and cyclization with the aim of preparing homologs of benzanthracene. γ-(5,6,7,8-Tetrahydro-2-naphthyl)-butyric acid, prepared by the literature method of condensation of tetralin with succinic anhydride followed by reduction of the keto-acid, was converted into the monosubstituted malonic ester (V) by condensation of its ethyl ester (IV) with diethyl oxalate and by thermal decarboxylation of the condensation product. Acid (I) was prepared from the substituted malonic ester (V) and 1,3-dichloro-2-butene by a three-step synthesis.



The product of interaction of acid (I) with sulfuric acid (s.g. 1.78) at 70-85°, obtained in 52.8% yield and forming a dinitrophenylhydrazone, corresponded in composition to formulas (II) and (III).

The ultraviolet absorption spectrum of the prepared ketone was plotted in the conditions described in the preceding paper [7]. The shape of the absorption curve of the ketone resembles that of benzylideneacetone [8] (Fig. 1), as was to be expected since a tetracyclic ketone, independently of whether it contains the cyclic skeleton of 1,2-benzanthracene (III) or 3,4-benzphenanthrene (II), must contain the conjugated double bond system of benzylideneacetone.

The maximum on the absorption curve of the tetracyclic ketone is shifted by approximately 30 mμ in the long-wave direction in comparison with the maximum of the benzylideneacetone curve. This circumstance, taking into consideration the existing literature data [8], must be explained by the fact that the investigated ketone is a β-substituted derivative of benzylideneacetone.

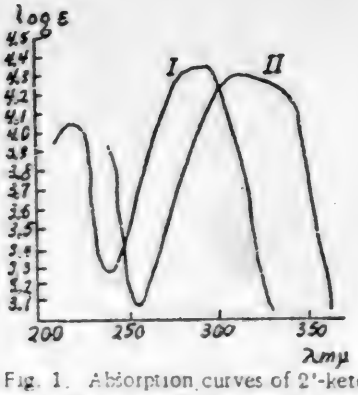


Fig. 1. Absorption curves of 2'-keto-decahydro-1,2-benzanthracene (II) and of benzylideneacetone (I) [8] in ethyl alcohol

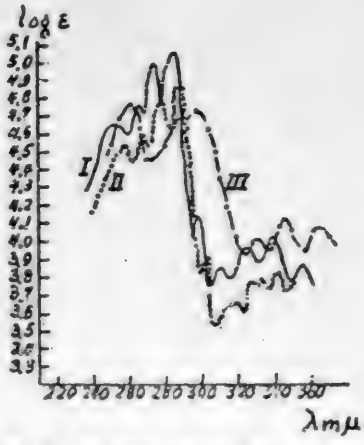


Fig. 2. Absorption curves of 1,2-benzanthracene (I), 2'-methylbenzanthracene (II) and 2'-phenylbenzanthracene (III) in ethyl alcohol.

The structure of the ketone was established by its dehydrogenation with platinized carbon; the main product of dehydrogenation was 1,2-benzanthracene (VIII), formed in a yield of 66.4% and identified as the picrate. A small amount of 2'-hydroxy-1,2-benzanthracene (IX) was also formed.

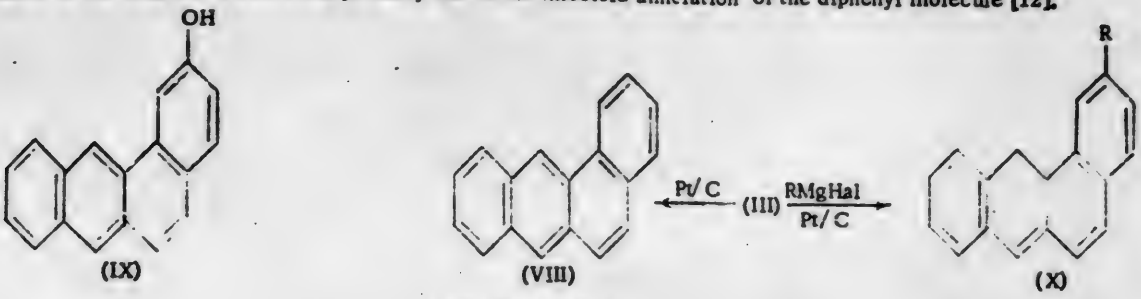
Organomagnesium compounds add on to the α,β-unsaturated ketone (III) exclusively in the 1,2 position, evidently due to the difficulty of addition of the alkyl group to the completely substituted and consequently difficultly accessible (from the steric aspect) β-carbon atom C_β. Reaction of the ketone with the appropriate Grignard reagents followed by dehydrogenation gave the previously described [9] 2'-methyl-1,2-benzanthracene and 2'-phenyl-1,2-benzanthracene (X) (the latter synthesized here for the first time).

These hydrocarbons were characterized in the form of picrates and maleic anhydride adducts.

The general shape and the position of the maxima of the ultraviolet absorption curves of benzanthracene and its 2'-methyl homolog (Fig. 2) are close to those of the parent hydrocarbon obtained by other authors [10].

In contrast to these hydrocarbons, the 2'-phenyl derivative has a curve similar to that of benzanthracene only in the long-wave region (310-360 mμ). In the short-wave region, however, the shape of the curve and the position of the maxima differ sharply from those of the other curves. This section of the curve is evidently associated with the presence of the diphenyl group as evidenced by the similarity of this section with the absorption curve of diphenyl

[11]. The maxima on this section of the curve, by comparison with the absorption curve of diphenyl, are sharply displaced in the long-wave direction, probably due to the threefold annelation of the diphenyl molecule [12].



EXPERIMENTAL

The initial β-(5,6,7,8-tetrahydro-2-naphthoyl)-propionic acid was prepared in 88.5% yield by condensation of tetralin with succinic anhydride [13]. Reduction of the keto acid with amalgamated zinc and hydrochloric acid [14] gave a 78% yield of the acid which distilled at 195-205° (6 mm) and crystallized completely in the receiver; m.p. 44-47°.

Ethyl γ-(5,6,7,8-tetrahydro-2-naphthyl)-butyrate (IV). A mixture of 175 g acid, 400 g absolute alcohol and 7.5 g conc. sulfuric acid was boiled under a reflux condenser for 7 hours; the greater part of the alcohol was then distilled off, 400 ml water was added and the product extracted with ether; the ethereal solution was washed with sodium carbonate solution, then with water and dried with anhydrous sodium sulfate. Removal of the solvent left 182 g (92.2% of the theoretical amount) of a colorless liquid with b.p. 160-165° at 4 mm.

d_4^{22} 1.0381; n_D^{22} 1.5348.

0.1054 g substance: 0.3090 g CO_2; 0.0862 g H_2O. 0.1016 g substance: 0.2911 g CO_2; 0.0816 g H_2O. Found %: C 78.40, 78.14; H 9.08, 8.92. $C_{16}H_{22}O_2$. Calculated %: C 78.05; H 8.94.

β-(5,6,7,8-Tetrahydro-2-naphthyl)-ethylmalonic ester (V). To a weighed amount of sodium alcoholate, prepared from 6.1 g sodium and 12.6 g absolute alcohol in 200 ml dry ether, was added a solution of 57 g diethyl oxalate in 50 ml absolute ether. After standing for an hour, gradual addition was made to the light-yellow solution, with stirring, of a solution of 64 g of ester (IV) in 50 ml dry ether. The mixture was gently boiled for 24 hours, after which it was cooled and decomposed with dilute sulfuric acid (15 ml conc. acid in 200 ml water). The ethereal solution of the reaction product was washed with water and dried with sodium sulfate. The oil remaining after removal of the ether was decarboxylated by heating in vacuum at a residual pressure of the order of 10-12 mm until the frothing due to evolution of carbon monoxide had ceased. After driving off the excess of ethyl oxalate and unreacted ester (IV), 55 g of a colorless, viscous oil with b.p. 194-195° at 2 mm was collected. Yield 55 g (66.4% of the theoretical).

d_4^{22} 1.0737; n_D^{22} 1.5230.

0.1027 g substance: 0.2710 g CO_2; 0.0758 g H_2O. Found %: C 71.97; H 8.20. $C_{19}H_{26}O_4$. Calculated %: C 71.69; H 8.17.

[β-(5,6,7,8-Tetrahydro-2-naphthyl)-ethyl-(3-chloro)-crotyl]-malonic ester (VI). To a solution of sodium alcoholate, prepared from 7.45 g sodium and 85 g absolute alcohol, was added 100 g of the mono-substituted malonic ester (V). After heating on the water bath for half an hour, the solution was cooled and gradual addition was made (with shaking) of 50 g freshly distilled 1,3-dichloro-2-butene. The mixture was refluxed for 5 hours; part of the alcohol was then distilled off; the residue was acidified, the product was dissolved in ether and the solution washed with water and dried with sodium sulfate. Distillation in vacuum gave 95.8 g (74.9% of the theoretical) of a thick, light-greenish liquid with b.p. 226-228° at 2 mm.

d_4^{23} 1.1080; n_D^{23} 1.5281.

0.1042 g substance: 0.0349 g AgCl. 0.1054 g substance: 0.0437 g AgCl. Found %: Cl 8.34, 8.59. $C_{23}H_{31}O_4Cl$. Calculated %: Cl 8.73.

[β-(5,6,7,8-Tetrahydro-2-naphthyl)-ethyl-(3-chloro)-crotyl]-malonic acid (VII). A mixture of 106 g ester (VI), 32 g NaOH and 440 g 90% alcohol was refluxed for 4 hours, after which 300 ml water was run in and the alcohol completely driven off. Acidification of the cooled solution with hydrochloric acid brought down a heavy,

yellowish oil. This was dissolved in ether and the solution washed and dried with sodium sulfate. After removal of the ether, the residue crystallized completely. Yield 85 g (93.0% of the theoretical) of colorless crystals with m.p. 137° after washing with benzene.

0.1026 g substance: 0.0430 g AgCl. 0.0911 g substance: 0.0374 g AgCl. Found %: Cl 10.43, 10.19. $C_{18}H_{23}O_4Cl$. Calculated %: Cl 10.12.

α-(3-Chlorocrotyl)-γ-(5,6,7,8-tetrahydro-2-naphthyl)-butyric acid (I). 65 g of the di-substituted malonic acid (VII) was decarboxylated by heating under reduced pressure. The resultant viscous oil was distilled in vacuum to give 53 g (93.24% of the theoretical) of a viscous, yellowish liquid with b.p. 216-218° at 1 mm.

d_4^{25} 1.1303; n_D^{25} 1.5598.

0.1054 g substance: 0.0493 g AgCl. 0.1021 g substance: 0.494 g AgCl. Found %: Cl 11.57, 11.97. $C_{18}H_{23}O_2Cl$. Calculated %:

2'-Keto-2,3,4,5,6,7,8,2',3',4'-decahydro-1,2-benzanthracene (III). To 15 ml sulfuric acid (s.g. 1.78) at room temperature was gradually added 3 g of the substituted butyric acid (I). Progressive addition was accompanied by deepening of the yellow color. Heating of the mixture on a water bath in a carbon dioxide stream initiated copious evolution of hydrochloric acid. The temperature was held at 70-80° for 3 hours until the substance had dissolved completely and hydrogen chloride had ceased to come off. The dark-red solution was then left overnight. Stirring of the reaction mixture with iced water caused separation of a viscous oil which crystallized completely on trituration. The substance was triturated with alkali solution, filtered, washed with water and dried. Recrystallization from alcohol gave 1.3 g (52.8% of the theoretical) of colorless crystals with m.p. 92-94°.

0.1006 g substance: 0.3155 g CO_2; 0.0732 g H_2O. 0.1004 g substance: 0.3152 g CO_2; 0.0730 g H_2O. Found %: C 85.53, 85.62; H 8.08, 8.07. $C_{18}H_{20}O$. Calculated %: C 85.71; H 7.93.

The bright-red 2,4-dinitrophenylhydrazone melted at 223-224° after recrystallization from a mixture of chloroform and alcohol. In spite of repeated recrystallization, the nitrogen content found for the substance was lower than the calculated value.

0.1026 g substance: 12.2 ml N_2 (28°, 576 mm). 0.1020 g substance: 12.2 ml N_2 (26°, 677 mm). Found %: N 12.10, 12.16. $C_{24}H_{24}O_4N_4$. Calculated %: N 12.96.

1,2-Benzanthracene (VIII). 3 g ketone (III) was dehydrogenated by heating with 1.2 g platinized carbon in a stream of carbon dioxide at 300-320° until hydrogen bubbles ceased to come off (about half an hour). The product was extracted with benzene; the benzene solution was washed with alkali, then with water and dried with sodium sulfate. Acidification of the washed alkali solution led to separation of a small amount of acid dehydrogenation product. The crystalline residue after removal of the benzene was obtained in the form of light-green leaflets with m.p. 159° after recrystallization from alcohol (boiled with carbon). The literature [15] reports m.p. 159-160°. Yield 1.8 g (66.4% of the theoretical).

0.1004 g substance: 0.3478 g CO_2; 0.0490 g H_2O. Found %: C 94.67; H 5.42. $C_{18}H_{12}$. Calculated %: C 94.73; H 5.26.

The dark-red picrate, isolated from benzene solution, had m.p. 133-134°.

0.1052 g substance: 9.2 ml N_2 (29°, 674 mm). Found %: N 8.79. $C_{24}H_{15}O_7N_3$. Calculated %: N 9.19.

2'-Hydroxy-1,2-benzanthracene (IX). The acid dehydrogenation product collected from three experiments on dehydrogenation of ketone (III) weighed 0.35 g after recrystallization from alcohol and was obtained in the form of light-green crystals with m.p. 186-188°.

0.1002 g substance: 0.3258 g CO_2; 0.0480 g H_2O. Found %: C 88.67; H 5.32. $C_{18}H_{12}O$. Calculated %: C 88.52; H 4.92.

2'-Methyl-1,2-benzanthracene (X, R=CH_3). To the Grignard solution prepared from 4 g Mg and 25 g methyl iodide was added, with stirring, an ethereal solution of 10 g ketone (III). After boiling for 2 hours, the cooled mixture was decomposed with dilute hydrochloride acid. The product was dissolved in ether, and the solution was washed with water and dried with sodium sulfate. Removal of the ether left 7.5 g yellow oil. 1.8 g of this oil was dehydrogenated with 0.3 g platinized carbon by heating for half an hour at 300-320° in a carbon dioxide atmosphere. The product was extracted with benzene and the solution washed with water and dried. The oil remaining after the benzene had been removed was dissolved in alcohol; slow evaporation of the latter left crystals with m.p. 142°. A

second recrystallization from alcohol (boiling with carbon) gave 0.9 g (55.2% of the theoretical, calculated on the intermediately formed oil) of colorless leaflets with m.p. 148°. The literature [9] reports m.p. 148-149° for 2'-methyl-1,2-benzanthracene.

Found %: C 94.07, 94.10; H 6.21, 6.19. $C_{19}H_{14}$. Calculated %: C 94.21; H 5.79.

The brick-red picrate, recrystallized from benzene, had m.p. 177° (the literature [9] reports m.p. 178-179°).

Found %: N 8.71. $C_{25}H_{17}O_7N_3$. Calculated %: N 8.91.

Like the picrate of benzanthracene itself, the picrates of benzanthracene homologs decompose into their components when attempts to recrystallize them from alcohol are made.

2'-Methyl-9,10-dihydro-1,2-benzanthracene-9,10-endo-α,β-succinic anhydride. A solution of 0.5 g 2'-methylbenzanthracene and 5 g freshly distilled maleic anhydride in 10 ml dry toluene are refluxed for 4 hours. The adduct which separated on cooling is filtered, washed several times with small portions of water, dried and recrystallized from benzene. M.p. 234-235°.

0.1049 g substance: 0.3115 g CO_2; 0.0492 g H_2O. Found %: C 80.98; H 5.21. $C_{23}H_{16}O_3$. Calculated %: C 81.14; H 4.74.

2'-Phenyl-1,2-benzanthracene (X, R = C_6H_5). Reaction of Grignard reagent, prepared from 3 g Mg and 20 g bromobenzene, with 10 g ketone (III) gave 9 g oily product. Dehydrogenation of 3.5 g of this oil with platinized carbon (0.6 g) and recrystallization from alcohol (boiling with carbon) gave 2.14 g (70% of the theoretical, calculated on the intermediately formed oil) of colorless crystals with m.p. 145°.

0.0574 g substance: 0.2000 g CO_2; 0.0284 g H_2O. Found %: C 95.02; H 5.49. $C_{24}H_{16}$. Calculated %: 94.73; H 5.26.

The picrate, prepared from benzene in the form of acicular crystals with a bright-red color, had m.p. 159-160°.

0.1037 g substance: 8.2 ml N_2 (25°, 676 mm). Found %: N 8.03. $C_{30}H_{19}O_7N_3$. Calculated %: N 7.88.

2'-Phenyl-9,10-dihydro-1,2-benzanthracene-9,10-endo-α,β-succinic acid. A solution of 5 g maleic anhydride in 12 ml dry toluene was boiled with 0.52 g hydrocarbon (X, R = C_6H_5) for 4 hours; the precipitate was filtered and thoroughly boiled several times with dilute sodium hydroxide solution. Acidification of the filtered alkaline solution brought down a white precipitate. The dried compound had m.p. 277-278°.

0.0716 g substance: 0.2100 g CO_2; 0.0350 g H_2O. Found %: C 79.98; H 5.43. $C_{28}H_{20}O_4$. Calculated %: C 79.97; H 4.89.

SUMMARY

1. It was found that α-(3-chlorocrotyl)-γ-(5,6,7,8-tetrahydro-2-naphthyl)-butyric acid, prepared from tetralin by a seven-step synthesis, undergoes hydrolysis and double cyclization when treated with sulfuric acid and forms a tetracyclic ketone with the carbon skeleton of 1,2-benzanthracene.

2. Dehydrogenation of the ketone and of the products of its interaction with Grignard reagents gave 1,2-benzanthracene and 2'-methyl- and 2'-phenyl-benzanthracenes.

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SYNTHESES IN THE 1,2-BENZANTHRACENE SERIES WITH THE AID OF LITHIUM REAGENTS

B. M. Mikhailov and T.K. Kozminskaya

In previous communications we described the application of organolithium compounds to the synthesis of derivatives of 1,2-benzanthracene [1] and 3,4'-ace-1,2-benzanthracene [2] with substituents in the 10-position. In the further development of this method of synthesis, which had proved extremely promising in the polycyclic series [3,4], we studied the transformations of organolithium compounds of 1,2-benzanthracene with substituents in the 4' and 4', 10-positions.

Reaction of bromine with 4'-bromo-1,2-benzanthracene leads to smooth bromination in the 10-position. An attempt was made to verify the structure of the obtained dibromo compound by treatment with one equivalent of phenyllithium and by hydrogenation of the resultant lithium derivative. This gave 4'-bromo-1,2-benzanthracene (I), which only indicated the greater reactivity of the newly-introduced bromine atom but not its position. The problem of the structure of the dibromo compound was solved in the following way: the lithium compound (III), prepared from the dibromo compound and phenyllithium, was methylated with methyl iodide. The methylbromo derivative (IV) in turn was treated with an excess of n-butyllithium and the resultant methyllithium compound (V) was hydrogenated. This gave 10-methyl-1,2-benzanthracene (VI), thus providing proof that the dibromo compound was 4', 10-dibromo-1,2-benzanthracene (II)

Reaction of an excess of n-butyllithium with 4', 10-dibromo-1,2-benzanthracene leads to substitution of both atoms of bromine by the metal. The dilithium compound of 1,2-benzanthracene (VII) reacts with methyl iodide to form 4', 10-dimethyl-1,2-benzanthracene. We also investigated the possibility of utilization of 4'-bromo-1,2-benzanthracene (I) for synthesis of 4'-derivatives. It was found that the bromo compound (I) reacts smoothly with n-butyllithium and the resultant 4'-lithium-1,2-benzanthracene (IX) can be successfully used for synthesis of 1,2-benzanthracene derivatives. Carboxylation of 4'-lithium-1,2-benzanthracene results in a good yield of 1,2-benzanthracene-4'-carboxylic acid (X). Reaction of the organolithium compound with methyl iodide gives smooth conversion to 4'-methyl-1,2-benzanthracene (XI).

Bromination of 4'-methyl-1,2-benzanthracene takes place in the 10-position. The structure of the dibromo compound (XII) was confirmed by transformation into 4', 10-dimethyl-1,2-benzanthracene (VIII). This was effected by treating 10-bromo-4'-methyl-1,2-benzanthracene with excess n-butyllithium and subjecting the resultant 4'-methyl-10-lithium-1,2-benzanthracene (XIII) to the action of methyl iodide. The so-obtained hydrocarbon was compared with a specimen of 4', 10-dimethyl-1,2-benzanthracene synthesized from 4',10-dibromo-1,2-benzanthracene. 4'-Methyl-10-bromo-1,2-benzanthracene, via the lithium compound (XIII), is readily converted with ethyl iodide or ethylene oxide into, respectively, 4'-methyl-10-ethyl- or 4'-methyl-10-β-hydroxyethyl-1,2-benzanthracene (XV)

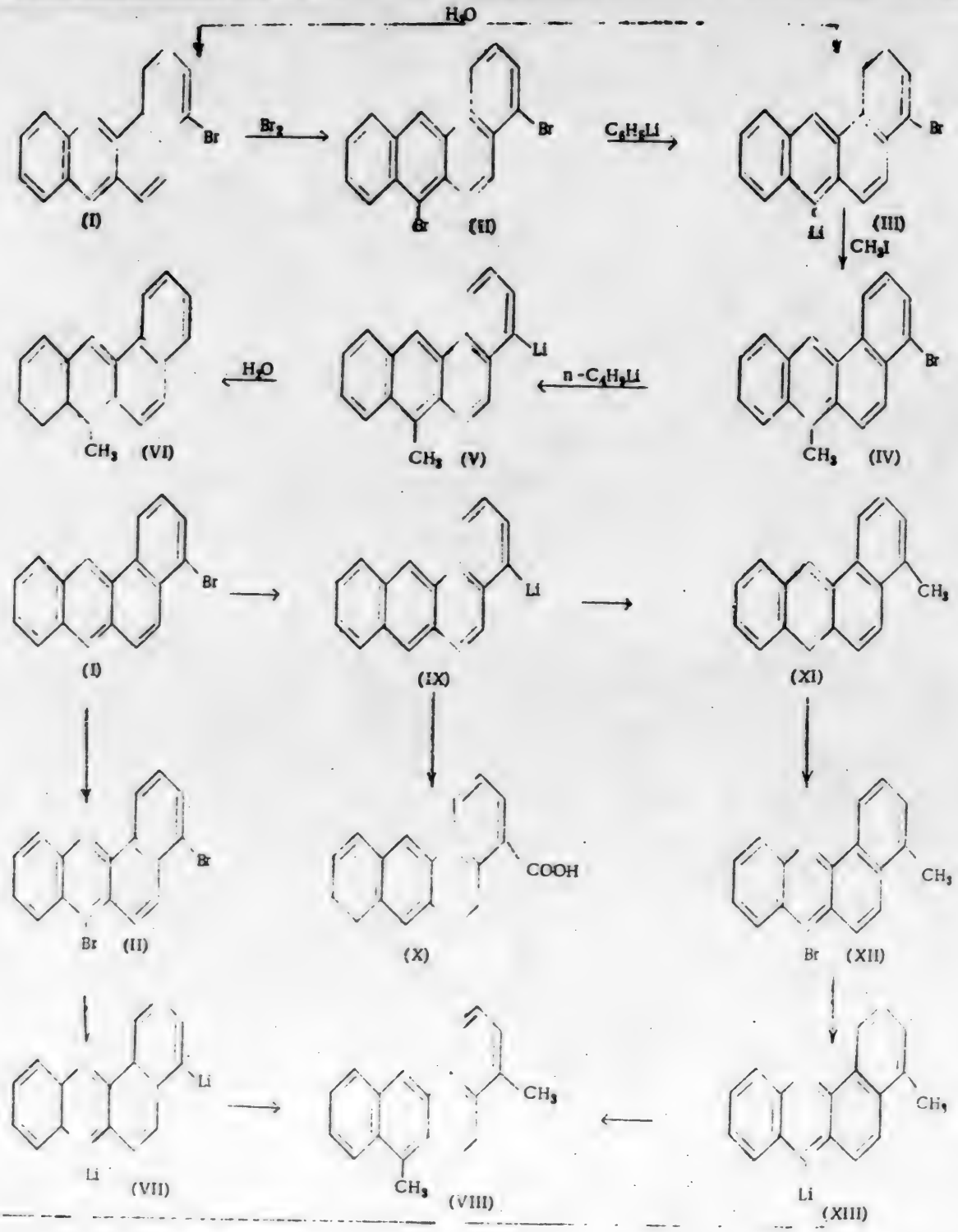
Carboxylation of 4'-methyl-1,2-benzanthryl-10-lithium gives smooth conversion to 4'-methyl-1,2-benzanthracene-10-carboxylic acid (XVI).

EXPERIMENTAL

4'-Bromo-1,2-benzanthracene (I). 1.5 g 4'-bromo-1,2-benzanthraquinone was dissolved in 150 ml glacial acetic acid, and to the solution was added 3 g tin chloride in 15 ml concentrated hydrocholoric acid. The reaction mixture was refluxed for an hour and poured into water the precipitate, quickly filtered at the pump, was washed with water. A small portion of the unrecrystallized 4'-bromo-1,2-benzanthrone was dried and analyzed.

5.437 mg substance: 13.031 mg CO_2; 1.768 mg H_2O. Found %: C 65.40, H 3.64; $C_{18}H_{11}OBr$. Calculated %: C 66.89; H 3.43.

The crude 4'-bromo-1,2-benzanthrone was quickly transferred to a flask and reduced by boiling for 1.5 hours with 15 ml of 2N NaOH and 1.5 g zinc dust. The cooled reaction mixture was filtered and the precipitate treated with dilute hydrochloric acid. The filtered and dried precipitate weighed 0.60 g and melted at 183-194°. Crystallization from acetic acid gave 0.41 g with m.p. 209-211° (30%). After one more recrystallization, 4'-bromo-1,2-


H2O
Br2
C6H5Li
(I)
(II)
(III)
CH3I
(IV)
n-C4H9Li
(V)
H2O
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(VII)
(VIII)
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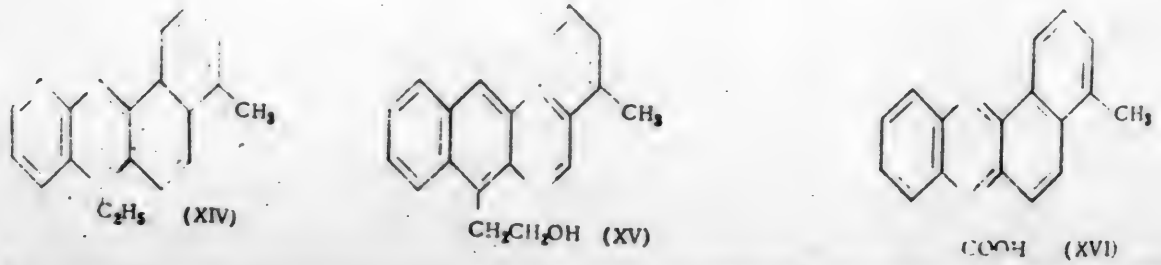
(XIV)
(XV)
(XVI)

benzanthracene melted at 210-211° in accord with the literature value [5].

From the combined mother liquors was isolated 0.32 g with m.p. 152-157.5°. After crystallization from benzene this substance melted at 158-160° and did not give a depression in admixture with a specimen of 1,2-benzanthracene.

Reduction of the same quantity of 4'-bromo-1,2-benzanthracene in other conditions failed to raise the yield and to avoid reduction of 4'-bromo-1,2-benzanthracene to hydrocarbon. The alternative conditions were: use of 10 g Zn dust and 100 ml 2 N NaOH, 1 g Zn dust and 10 ml 2 N NaOH at the boil for 1 to 3 hours, activation of the zinc with copper sulfate, replacement of alkali by ammonia, and operation in presence of toluene.

Clemmensen reduction of the bromobenzanthrone led to negative results.

4', 10-Dibromo-1,2-benzanthracene (II). 1 g 4'-bromo-1,2-benzanthracene was dissolved by heating in 100 ml carbon tetrachloride. The hot solution was brominated by dropwise addition of 0.7 g bromine (20% excess) dissolved in 20 ml carbon tetrachloride. The reaction mixture, containing the precipitate, was heated to the boil. The precipitate dissolved completely. The reaction mixture was left overnight at room temperature. After driving off the solvent, the residue was crystallized from benzene to give 0.98 g greyish long, slender needles with m.p. 192-193.5°. The yield of dibromo compound was 78.4% of the theoretical. After repeated crystallizations from benzene and isoamyl ether, 4',10-dibromo-1,2-benzanthracene melted at 194.5-195.5°.

4.863 mg substance: 9.931 mg CO_2; 1.153 mg H_2O. Found %: C 55.73; H 2.65. $C_{18}H_{10}Br_2$. Calculated %: C 56.00; H 2.61.

10-Methyl-1,2-benzanthracene. 9 ml of an ethereal solution of phenyllithium (0.375 N), i.e., 1.3 moles, was run into a weighed amount (1 g) of dibromo compound (II) in 30 ml dry benzene. After brief shaking the precipitate of dibromo compound went into solution. 2 g methyl iodide was added to the reaction mixture. After 2 hours, the reaction products were poured into water; the solvent was driven off from the upper layer and the residue recrystallized from benzene. 0.62 g crystals with m.p. 178-181° was obtained. The m.p. rose to 182-183° after crystallization from ethyl acetate: the crystals under the microscope had the appearance of colorless rhombic platelets. The analysis accords with 4'-bromo-10-methyl-1,2-benzanthracene. Due to the solubility being similar to that of both the original bromo compound and 4',10-dimethyl-1,2-benzanthracene, the prepared compound cannot be easily freed from impurities.

5.068 mg substance: 12.866 mg CO_2; 1.755 mg H_2O. Found %: C 69.28; H 3.87. $C_{19}H_{13}Br$. Calculated %: C 71.05; H 4.08.

To 0.5 g of the prepared product, dissolved in 10 ml dry benzene, was added an ethereal solution of n-butyllithium prepared from 0.25 g n-butyl chloride. The reaction mixture was treated with water and the residue (following removal of solvent) was dissolved in ligroin and passed through alumina. 0.15 g substance was obtained with m.p. 134-137° (40%). After two crystallizations from ethanol it melted at 139-140° and did not give a depression with a specimen of 10-methyl-1,2-benzanthracene.

A solution in benzene-ether of the 4'-bromo-10-lithium-1,2-benzanthracene prepared by the above method from 0.5 g 4',10-dibromo-1,2-benzanthracene was poured into water. The layers were separated and the solvent was driven off from the upper layer. The residue was crystallized from benzene to give 0.16 g with m. p. 210-212°. A mixed test with a specimen of 4'-bromo-1,2-benzanthracene did not show a melting point depression. Yield 40% of the theoretical. A pure substance could not be isolated from the mother liquor.

4',10-Dimethyl-1,2-benzanthracene (VIII). The reaction between 0.5 g 4',10-dibromo-1,2-benzanthracene (dissolved in 40 ml dry benzene) and an ethereal solution of n-butyllithium (prepared from 0.5 g n-butyl chloride and 0.1 g metallic lithium) was continued for half an hour. After addition of 2.5 g methyl iodide over a period of 2 hours, the reaction mixture was treated with water and the solvent was driven off from the ether-benzene layer. The residue was crystallized from benzene and then from ethanol, giving 0.16 g crystals (48.4%) melting at 153-154°. The pure compound melts at 154-154.5°.

4.756 mg substance: 16.284 mg CO_2; 2.520 mg H_2O. 4.686 mg substance: 16.076 mg CO_2; 2.508 mg H_2O. Found %: C 93.64, 93.94; H 5.93, 5.98. $C_{20}H_{16}$. Calculated %: C 93.71, H 6.29.

1,2-Benzanthracene-4'-carboxylic acid (X). To an ethereal solution of n-butyllithium, prepared in the usual way from 0.25 g n-butyl chloride and 0.05 g lithium, was added a benzene solution of 0.5 g 4'-bromo-1,2-benzanthracene (40 ml). After 10 minutes, the reaction mixture was poured onto solid carbon dioxide and treated with water. Acidification of the filtered, alkaline aqueous layer gave 0.27 g light-yellow substance melting at 280-285° (yield 61.4% of the theretical). After crystallization from ethanol, 1,2-benzanthracene-4'-carboxylic acid melts at 286°.

4.759 mg substance: 14.032 mg CO_2; 2.32 mg H_2O. Found %: C 83.73; H 4.76. $C_{19}H_{12}O_2$. Calculated %: C 83.80; H 4.44.

A solid melting at 138-143° was isolated from the ether-benzene layer; it was impossible to isolate pure substances.

4'-Methyl-1,2-benzanthracene (XI). To an ether-benzene solution of 1,2-benzanthryl-4'-lithium, prepared from 2 g 4'-bromo-1,2-benzanthracene, was added an ethereal solution of 3 g methyl iodide. The color of the reaction mixture became light-yellow. At the expiration of 2 hours, water was added to the reaction mixture; the solvent was driven off from the ether-benzene layer and the residue was crystallized from benzene to give 1.13 g colorless platelets melting at 192-194°. Yield 72% of the theoretical. After a second crystallization from the same solvent, 4'-methyl-1,2-benzanthracene melted at 194-195° in agreement with the literature [6].

3.338 mg substance: 11.550 mg CO_2; 1.793 mg H_2O. Found %: C 94.42; H6.01. $C_{19}H_{14}$. Calculated %: C 94.18; H 5.82.

4'-Methyl-10-bromo-1,2-benzanthracene (XII). 2 g 4'-methyl-1,2-benzanthracene was dissolved in 100 ml carbon bisulfide. Dropwise addition was slowly made to the solution of 1.62 g bromine (20% excess) dissolved in 40 ml carbon bisulfide. The reaction mixture was left overnight. The carbon bisulfide was driven off and the residue crystallized from benzene to give 1.9 g substance with m.p. 155-161°. After crystallization from benzene-ethanol, 1.7 g (60.4%) of substance with m.p. 158-162° was obtained. Recrystallization of the 4'-methyl-10-bromo-1,2-benzanthracene from ethyl acetate raised the m.p. to 162-164°.

6.112 mg substance: 15.924 mg CO_2; 2.284 mg H_2O. Found %: C 71.10; H 4.18. $C_{19}H_{12}Br$ Calculated %: C 71.04; H 4.07.

4',10-Dimethyl-1,2-benzanthracene from 4'-methyl-10-bromo-1,2-benzanthracene 0.75 g 4'-methyl-10-bromo-1,2-benzanthracene, dissolved in 22 ml dry benzene, was added to an ethereal solution of n-butyllithium prepared from 0.4 g n-butyl chloride. After 15 minutes an ethereal solution of 1.2 g methyl iodide was run into the brown-colored reaction mixture. Slight heat was developed and the reaction mixture gradually became lighter in color. After two hours the mass was worked up in the usual manner and the solid recovered from the ether-benzene layer was crystallized from benzene and ethanol to give 0.25 g of white, fluffy needles melting at 153.5-154.5°. The yield was 62.5 % of the theoretical. The substance does not give a depression of m.p. with a specimen of 4,10-dimethyl-1,2-benzanthracene that we prepared by another route.

4'-Methyl-1,2-benzanthracene-10-carboxylic acid (XVI). After 10 minutes' reaction between a benzene solution of 2 g 4'-methyl-10-bromo-1,2-benzanthracene and an ethereal solution of n-butyllithium, the reaction mixture was carboxylated. The cloudy aqueous layer was made alkaline, boiled to remove ether, and filtered. From the acidified filtrate with acetic acid was obtained an acid melting at 236-240°. Yield 85.4% of the theoretical.

4.465 mg substance: 13.69 mg CO_2; 2.119 mg H_2O. Found %: C 83.68; H 5.31. $C_{20}H_{14}O_2$. Calculated %: C 83.89; H 4.93.

From the ether-benzene layer was isolated only 0.06 g of an oily product.

4'-Methyl-10-ethyl-1,2-benzanthracene (XIV). In similar conditions isolation was effected of 0.14 g substance with m.p. 194-197° from 0.5 g 4'-methyl-10-bromo-1,2-benzanthracene. Yield 33.3% of the theoretical. After crystallization from benzene and from ethanol, 4'-methyl-10-ethyl-1,2-benzanthracene melted at 198-199°. Under the microscope it had the form of fine, colorless prisms.

6.71 mg substance: 23.00 mg CO_2; 4.01 mg H_2O. Found %: C 93.54; H 6.64. $C_{21}H_{18}$. Calculated %: C 93.29; H 6.71.

4'-Methyl-10-β-hydroxyethyl-1,2-benzanthracene (XV) Reaction of gaseous ethylene oxide with an ether-benzene solution of 4'-methyl-1,2-benzanthryl-10-lithium (prepared from 0.5 g dibromo compound) gave crystals melting at 157-160° (from benzene). Yield 84 %. A second crystallization from ethanol gave 4'-methyl-10-β-hydroxyethyl-1,2-benzanthracene in the form of colorless, fluffy needles with m.p. 159-160.5°.

6.04 mg substance: 19.46 mg CO_2; 3.47 mg H_2O. Found %: C 87.92; H 6.43. Calculated %: C 88.07; H 6.34.

SUMMARY

1. 4'-Bromo- and 4'-methyl-1,2-benzanthracene undergo bromination in the 10-position.

2. 4'-Bromo- and 4'-methyl-10-bromo-1,2-benzanthracene are smoothly transformed into organolithium compounds applicable to the syntheses of the corresponding derivatives of 1,2-benzanthracene.

3. 4',10-Dibromo-1,2-benzanthracene when treated with excess of n-butyllithium forms 4',10-dilithium-1,2-benzanthracene, which is suitable for the synthesis of 4',10-disubstituted 1,2-benzanthracenes.

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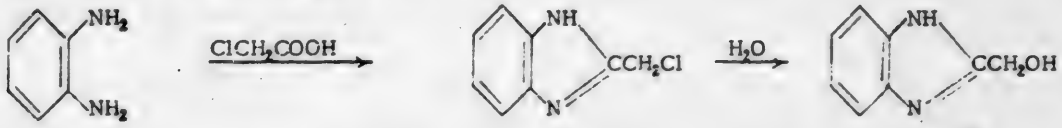
**** " " " " " 1659.

IMIDAZOLE DERIVATIVES

X. ACYLATION OF 2-HYDROXYMETHYLBENZIMIDAZOLE AND THE PRODUCTS OF ITS METHYLATION

N. A. Zakharova, B. A. Porai-Koshits, and L. S. Efros

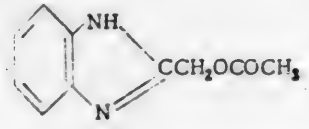
Many esters formed from aminoalchohols and organic acids are physiologically active compounds. Since benzimidazole derivatives frequently exhibit such properties, it seemed of interest to prepare a series of such esters, using a benzimidazole derivative as the aminoalcohol, namely 2-hydroxymethylbenzimidazole (I). We prepared this compound by the following route [1,2,3]:



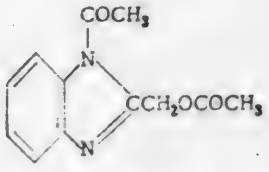
(I)

Acetylation of compound (I) with acetic anhydride in presence of anhydrous sodium acetate was carried out by Bystrzhitsky and Przhevorsky [4] who obtained a product which they assumed to be 2-acetoxymethylbenzimidazole (II).

In actuality, as we established in the present investigation, this compound is a diacetyl derivative and has the structure (III).

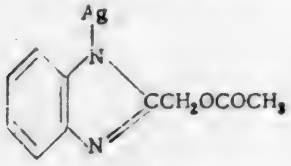


(II)



(III)

The monoacetyl derivative (II) in which we are interested is obtained by performing the acylation reaction in slightly different conditions (omission of sodium acetate). The structure of the substance (II) that we prepared was confirmed by synthesis of its silver salt (IV) and iodoamine (V).



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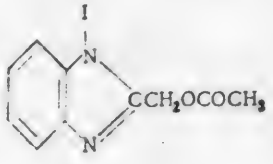
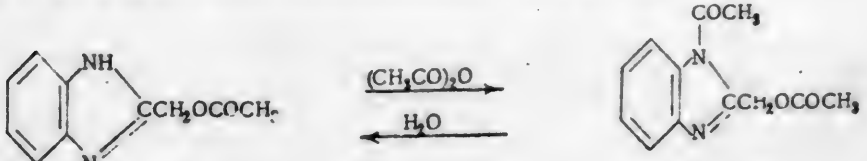


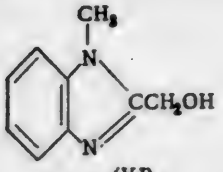
(V)

Further acylation of 2-acetoxymethylbenzimidazole leads to the diacetyl derivative (the reaction is reversible)



(II) (III)

Consequently it is clear that in the acetylation of 2-hydroxymethylbenzimidazole, the reaction proceeds first at the hydroxyl group of this compound and subsequently a diacetyl compound is obtained in which the second radical of the organic acid is bound to one of the nitrogen atoms of the heterocycle. With the aim of obtaining conclusive evidence of the correctness of our theory of the course of the acetylation reaction and of confirming our suggested formula for the Bystrzhitsky product, we decided to acetylate 1-methyl-2-hydroxymethy benzimidazole (VI).

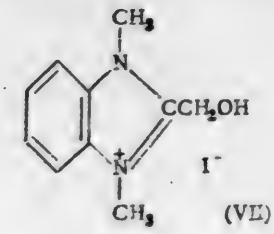


(VI)

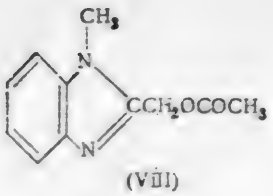
In this case acetylation could theoretically result in formation of only one compound — the product of substitution of the hydrogen of the hydroxy group. The inability of the prepared monoacetyl derivative to undergo further acetylation was indirectly confirmed by the fact that the second acetyl group enters the nitrogen heterocycle when the acetylation of monoacetoxymethylbenzimidazole is performed.

1-Methyl-2-hydroxybenzimidazole was prepared by the action of methyl iodide on 2-hydroxymethybenzimidazole in an alcoholic medium under pressure. Apart from this product, all the methylation experiments gave greater of lesser amounts of the methoiodide of 1-methyl-1-hydroxymethylbenzimidazole (VII). Raising the reaction temperature to above 120° results in a secondary reaction of reduction of the alcohol group. The separation of the components formed on methylation of 2-hydroxymethylbenzimidazole presented some experimental difficulties.

Acetylation of 1-methyl-2-hydroxymethylbenzimidazole gave, as anticipated, only the monoacetyl derivative (VIII), which is incapable of entering into further reaction with acetic anhydride.

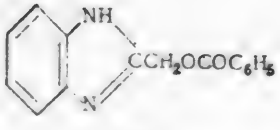


(VII)

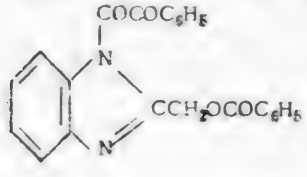


(VIII)

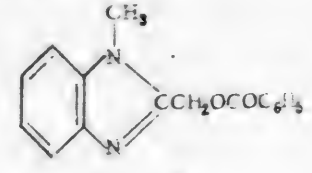
Benzoylation proceeds on precisely the same lines for 2-hydroxymethylbenzimidazole and for 1-methyl-2-hydroxymethylbenzimidazole. 2-Hydroxymethylbenzimidazole is benzoylated, like benzimidazole, in a pyridine medium [5] or a chlorobenzene medium. The reaction leads to a mixture of the mono- and dibenzoyl-derivatives (IX) and (X) and to an oily product whose structure was not established. The structure of the monobenzoyl derivative was confirmed by analysis and by the preparation of its silver salt whose structure is similar to that of (IV). Benzoylation of 1-methyl-2-hydroxymethylbenzimidazole gives a good yield of the corresponding ester (XI).



(IX)



(X)



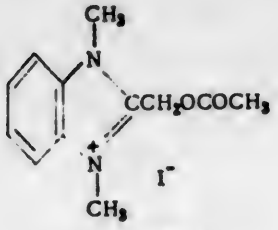
(XI)

The above-described reaction proceeded with considerably greater difficulty in the case of 1-methyl-2-hydroxymethylbenzimidazole methoiodide (VIII). In certain conditions it was possible to obtain and purify the derivative (XII), whereas we failed to obtain the benzoyl derivative and the starting material was recovered from the reaction mixture.

EXPERIMENTAL

1. Preparation of 2-hydroxymethylbenzimidazole and the products of its methylation. a) 2-Hydroxymethylbenzimidazole. Preparation was effected by hydrolysis of 2-chloromethylbenzimidazole [3] in a yield of 65-73.6%. The latter was synthesized by condensation of o-phenylenediamine with monochloracetic acid in a dilute hydrochloric acid medium [1,2]. The yield of product was 75-83% of the theoretical.

b) Methylation of 2-hydroxymethylbenzimidazole. A mixture of 5 g 2-hydroxymethylbenzimidazole, 5.6 ml methyl iodide and 5 ml absolute methyl aclohol is heated in a sealed tube at 70-90° for 5 hours. The precipitate (6.35 g) is filtered off; it consists of the hydroiodide of 1-methyl-2-hydroxymethylbenzimidazole and its methoiodide. It is dissolved in 10-15 ml water and, under ice cooling, addition is made of ammonia until the reaction is alkaline. A mixture of 1-methyl-2-hydroxymethylbenzimidazole (base) and the salt of the quaternary compound comes down. The precipitate is filtered and dried; weight 3.86 g. After drying, it is treated in 3 portions with 250 ml absolute benzene. The residue after treatment is 1.3 g of the methoiodide of 1-methyl-2-hydroxymethylbenzimidazole; the base goes into solution. The alcoholic filtrate from the reaction tube is evaporated to dryness, giving 2.9 g solid material. This is worked up as described above with water, ammonia and benzene; 0.9 g methoiodide remains undissolved.



(XII)

The benzene solutions are combined and the benzene is driven off to leave 1.8 g of 1-methyl-2-hydroxymethylbenzimidazole base. Two crystallizations from benzene give 1.2 g with m.p. 146-147° (yield 20.1% of the theoretical).

The ammoniacal filtrates are combined and evaporated to dryness; the residue is worked up with a small quantity of boiling absolute ethyl alcohol; on cooling, 0.8 g methoiodide is obtained. All the precipitates of quaternary base are combined and crystallized twice from absolute alcohol. 2.09 g of the methoiodide of 1-methyl-2-hydroxymethylbenzimidazole is obtained with m.p. 187-188° (20.35%). The mixture of salts of the tertiary and quaternary bases can also be separated by repeated crystallization from alcohol, but the yield of products is then very low.

1-Methyl-2-hydroxymethylbenzimidazole. White crystals with m.p. 146-147°.

0.1092 g substance: 16.6 ml N_2 (20°, 752 mm). 0.0985 g substance: 14.65 ml N_2 (21°, 759 ml). Found %: N 17.53, 1725 $C_9H_{10}ON_2$. Calculated %: N 17.28.

The hydrochloride is obtained by passing dry hydrogen chloride through a solution of the base in absolute alcohol and precipitating the salt with absolute ether. M.p. 189-190°.

0.2430 g substance: 0.1765 g AgCl. 0.2325 g substance: 0.1654 g AgCl. Found %: Cl 17.96, 17.60. $C_9H_{11}ON_2Cl$. Calculated %: Cl 17.85

The hydroiodide has an unsharp melting point.

0.1032 g substance: 8.7 ml N_2 (19°, 760 mm). 0.1149 g substance: 9.45 ml N_2 (20°, 769 mm). 0.2244 g substance: 0.1795 g AgI. Found %: N 9.87, 9.70; I 43.24. $C_9H_{11}ON_2I$. Calculated %: N 9.66; I 43.75.

Methoiodide of 1-methyl-2-hydroxymethylbenzimidazole. Colorless or greenish lustrous needles with m.p. 187-188°.

0.1309 g substance: 10.9 ml N_2 (20°, 747 mm). 0.1183 g substance: 9.4 ml N_2 (21°, 770 mm). 0.2132 g substance: 0.1643 g AgI. 0.2726 g substance: 0.2093 g AgI. Found %: N 9.54, 9.34; I 41.66, 41.50. $C_{10}H_{13}ON_2I$. Calculated %: N 9.21; I 41.73.

Methylation of 2.4 g 2-hydroxymethyl benzimidazole base gave 4.4 g product which after crystallization from water or 10% ammonia gave 3.8 g methoiodide of 1,2-dimethylbenzimidazole with m.p. 258-259° [6].

Found %: I 44.22, 44.13. $C_{10}H_{13}N_2I$. Calculated %: I 44.05.

The same compound was synthesized from 2-methylbenzimidazole. In the above-described conditions, 2.6 g (0.02 mole) base of 2-methylbenzimidazole gives 3.85 g crude product which after two crystallizations gives 2.7 g lustrous needles with m.p. 257-258°. Both in properties and in outward appearance, this product was identical with the one described above. A mixed sample gave m.p. 258-259°.

2. Acetylation of 2-hydroxymethylbenzimidazole and of the products of its methylation. a) 2-Acetoxymethylbenzimidazole. 7 g (0.05 mole) 2-hydroxymethylbenzimidazole, 9.45 ml (0.1 mole) acetic anhydride and 10 ml glacial acetic acid are heated on a boiling water bath for 30-40 minutes; the solution is then evaporated to dryness, giving 8.95 g (98.7%) crude product. Two crystallizations from benzene or water give 6.3 g white prisms with m.p. 163-164°.

0.2044 g substance: 26.6 ml N_2 (22°, 756 mm). 0.1787 g substance: 23.4 ml N_2 (22°, 752 mm). 0.0261 g substance: 6.87 ml 0.02 N NaOH. 0.0302 g substance: 7.88 ml 0.02 N NaOH. Found %: N 14.98, 14.99; acetyl groups 22.65, 22.47. $C_{10}H_{10}O_2N_2$. Calculated %: N 14.73; acetyl groups 22.63.

The compound is poorly soluble in gasoline, better in water, readily soluble in alcohol. Boiling with 0.1 N hydrochloric acid and 0.1 N caustic alkali leads to saponification of the acetyl radical and to formation of 2-hydroxymethylbenzimidazole. Heating with boiling glacial acetic acid does not modify the compound, whereas heating with acetic anhydride for 20-25 minutes leads to formation of 1-acetyl-2-acetoxymethylbenzimidazole, which after crystallization from a mixture of gasoline and benzene melts at 97-98°.

Silver salt. 1.5 g of 2-acetoxymethylbenzimidazole is dissolved in 15 ml alcohol; a solution of 1.5 g silver nitrate in 5 ml water, to which 5 ml concentrated aqueous ammonia has previously been added, is run in. The resultant precipitate is filtered and washed with alcohol and water. Yield 2.32 g (theoretical) of fine white crystals.

0.3311 g substance: 0.1199 g Ag. 0.4233 g substance: 0.1528 g Ag. Found %: Ag 36.21, 36.10. $C_{10}H_9O_2N_2Ag$. Calculated %: Ag 36.32.

Iodoamine. 0.5 g 2-acetoxymethylbenzimidazole is dissolved in 150 ml hot water; to the ice-cooled solution is added 4 ml 25% NaOH and (dropwise with constant stirring) 52.1 ml (the theoretical amount) of 0.1 N solution of iodine in potassium iodide. Yield 0.82 g white amorphous powder with m.p. 164° (with decomposition). The percentage content of iodine in the obtained product is determined iodometrically. A weighed amount of about 0.5 g 1-iodo-2-acetoxymethylbenzimidazole is introduced into a 250 ml measuring flask; 60 ml 10% KI solution and 25 ml 2 N hydrochloric acid are added. The contents are thoroughly shaken and gently heated to dissolve the precipitated black flocs. The transparent solution is made up to the mark with water. Titration is performed on 50 ml amounts of the solution.

0.4479 g substance: titration of 50 ml solution took on the average 5.56 ml 0.1 N $Na_2S_2O_3$. Found %: I 39.38. $C_{10}H_9O_2N_2I$. Calculated %: I 40.15.

b) 1-Acetyl-2-acetoxymethylbenzimidazole. To 5 g 2-hydroxymethylbenzimidazole is added 5 g anhydrous sodium acetate in 20 ml acetic anhydride. The mixture is heated on a boiling water bath for 20 minutes. The liquid reagents are removed by evaporation and the residual crystalline mass is treated with a small quantity of ligroin. Yield 6.62 g (84%) of white prisms with m.p. 96-98°. After crystallization from a mixture of gasoline and benzene, the m.p. was 98-99.5°.

0.2111 g substance: 22.6 ml N_2 (21°, 760 mm). 0.1523 g substance: 16.4 ml N_2 (21°, 760 mm). 0.0359 g substance: 15.23 ml 0.02 N NaOH. Found %: N 12.43, 12.50, acetyl groups 36.53. $C_{12}H_{12}O_3N_2$. Calculated %: N 12.06; acetyl groups 37.97.

The substance is sparingly soluble in water, alcohol, and gasoline, slightly better in benzene. Boiling with water for 10 minutes results in a quantitative yield of 2-acetoxymethylbenzimidazole with m.p. 163-164°. On prolonged storage the product decomposes.

c) 1-Methyl-2-acetoxymethylbenzimidazole. A mixture of 3.2 g 1-methyl-2-hydroxymethylbenzimidazole, 2.5 ml (30% excess) acetic anhydride, and 7 ml glacial acetic acid is heated for an hour on a boiling water bath. The liquid is evaporated to dryness; the resultant yellow oil is worked up with absolute ether to give 2.54 g (63%) of a white substance which after two crystallizations from a 3:1 mixture of gasoline and benzene gives white needles with m.p. 76-78°.

0.1190 g substance: 14.2 ml N_2 (20°, 757 mm). 0.1039 g substance: 12.2 ml N_2 (20°, 764 mm). Found %: N 13.84, 13.75. $C_{11}H_{12}O_2N_2$. Calculated %: N 13.72.

d) Acetylation of the methiodide of 1-methyl-2-hydroxymethylbenzimidazole. 6 g (0.02 mole) methiodide of 1-methyl-2-hydroxymethylbenzimidazole, 2.6 ml (30% excess) acetic anhydride, and 10 ml glacial acetic acid are heated on a boiling water bath for 1.5 hour. The dark red crystals (3.8 g) are filtered off; to the filtrate is added absolute ether; a yellow oil is precipitated and is converted into a white solid after two treatments with absolute ether and chloroform; after two crystallizations from the minimum volume of absolute alcohol, it gives 0.4 g product with m.p. 256-258° (with decomposition). The 3.8 g of filtered dark crystals is treated with 60-70 ml dry chloroform; a large proportion goes into solution, leaving 0.28 g of the above-described by-product. The chloroform solution is washed with a small quantity of an aqueous solution of thiosulfate in order to remove iodine; the water is separated; the chloroform layer is dried with calcium chloride and the solvent is driven off, leaving 1.65 g of a substance which, after three crystallizations from absolute alcohol gave about 0.5 g pinkish leaflets with constant m.p. of 164-165°.

0.1697 g substance: 0.1141 g AgI. 0.1659 g substance: 0.1120 g AgI. Found %: I 36.35, 36.50. $C_{12}H_{15}O_2N_2I$. Calculated %: I 36.67.

Analysis of the high-melting by-product with m.p. 256-258° gave the following results.

0.1289 g substance: 0.1029 g AgI. 0.1211 g substance: 0.0966 g AgI. Found %: I 43.15, 43.12.

3. Benzoylation of 2-hydroxymethylbenzimidazole and of the products of its methylation.

a) Benzoylation of 2-hydroxymethylbenzimidazole. Benzoylation is effected in a chlorobenzene medium by

the action of benzoyl chloride on the hydrochloride of 2-hydroxymethylbenzimidazole. 5.4 g (0.03 mole) thoroughly ly dried and pulverized 2-hydroxymethylbenzimidazole hydrochloride is suspended in 100 ml boiling chlorobenzene and dropwise addition is made of 4.1 ml (5.0g, 20% excess) benzoyl chloride in 15 ml chlorobenzene. After boiling for 6 hours, the mass is cooled and the precipitate filtered off. Yield 4.88 g (57.7%) of 2-benzoylhydroxymethylbenzimidazole; . it is washed with pure chlorobenzene. The filtrate and wash liquor are combined and the chlorobenzene is distilled off to leave a small amount of oil which partially solidified after 24 hours. Ether extraction removed 2.0 g unsolidified oil, leaving 1.46 g (14.5% of theoretical) of 1-benzoyl-2-benzoylhydroxymethylbenzimidazole.

2-Benzoylhydroxymethylbenzimidazole. White, lustrous hexagonal leaflets with m.p. 146-147°. Crystallizes from aqueous alcohol or from a mixture of benzene and gasoline. Soluble in alcohol, benzene and acetone; insoluble in water and gasoline.

0.1272 g substance: 0.3342 g CO_2; 0.0557 g H_2O. 0.1356g substance: 0.3563 g CO_2; 0.0584 g H_2O. 0.2257 g substance: 32.46 ml 0.1 N. NaOH. 0.2409 g substance: 31.23 ml 0.1 N NaOH. 0.0258 g substance: 5.09 ml 0.02 N NaOH. 0.0237 g substance: 4.73 ml 0.02 N NaOH. Found %: C 71.65, 71.67 H 4.99, 4.82; N 10.97, 10.99 (Kjeldahl); benzoyl groups 41.47, 41.95. $C_{15}H_{12}O_2N_2$. Calculated %: C 71.43; H 4.80; N 11.11; benzoyl groups 41.66.

The base is not saponified by dilute inorganic acids; boiling with 4 N hydrochloric acid leads to the hydrochloride with m.p. 233-235°; crystallizes from water or alcohol.

0.0682 g substance: 0.0337 g AgCl. 0.1975 g substance: 0.0968 g AgCl. Found % Cl 12.22, 12.13. $C_{15}H_{15}O_2N_2Cl$. Calculated %: Cl 12.28.

Boiling with 4 N sulfuric acid gives the acid sulfate in the form of white, lustrous crystals with m.p. 207-210°; purified by crystalization from dilute sulfuric acid.

0.5638 g substance. 0.3794 g $BaSO_4$. 0.4431 g substance: 0.2968 g $BaSO_4$. Found %: S 9.25, 9.20. $C_{15}H_{16}O_6N_2S$. Calculated %: S 9.15.

The silver salt was prepared in conditions similar to those for the salt of 2-acetoxymethylbenzimidazole. White crystals; yield 88.8% of the theoretical.

0.2964 g substance: 0.0888 g Ag. 0.3010 g substance: 0.0992 g Ag. Found %: 29.96, 29.97. $C_{15}H_{11}O_2N_2Ag$. Calculated %: Ag 30.04.

1-Benzoyl-2-benzoylhydroxymethylbenzimidazole. White, irregularly shaped crystals with m.p. 89-91°, soluble in alcohol, acetone and benzene; insoluble in water gasoline, ether and dilute hydrochloric and sulfuric acids; it decomposes when boiled with inorganic acids with formation of salts of 2-benzoylhydroxymethylbenzimidazole.

0.1522 g substance: 21.17 ml 0.1 N NaOH. 0.5148 g substance: 29.97 ml 0.1 N NaOH. 0.0216 g substance: 6.30 ml 0.02 N NaOH. 0.0230 g substance: 6.68 ml 0.02N NaOH. Found %: N 8.02, 8.03 (Kjeldahl); benzoyl groups 61.31, 61.05. $C_{21}H_{16}O_3N_2$. Calculated %. N 8.14; benzoyl groups 61.65.

The dark yellow oil formed during benzoylation is soluble in acetone, methyl and ethyl alcohols, benzene, toluene, pyridine, ether and chloroform; less soluble in gasoline, insoluble in water. Treatment in the cold with 4 N hydrochloric acid converts it into the hydrochloride of 2-benzoylhydroxymethylbenzimidazole, and benzoyl chloride and benzoic acid are separated. A similar decomposition is observed on lengthy standing of the oil in the air or on heating at 80-100°. The nitrogen determination (Kjeldahl) gave the following result:

0.4352 g substance: 34.00 ml 0.1 N NaOH. 0.5844 g substance: 27.89 ml 0.1 N NaOH. Found %: N 5.31, 5.42.

b) Benzoylation of 1-methyl-2-hydroxymethylbenzimidazole. To 3.24 g (0.02 mole) 1-methyl-2-hydroxymethylbenzimidazole suspended in 40 ml absolute benzene, 3.4 g (2.8 ml, 20% excess) benzoyl chloride in 10 ml absolute benzene is added. The mixture is heated at the boil for an hour, cooled, and filtered; the precipitate is repeatedly washed with pure absolute benzene to give 4.88-5.12 g (80.9-84.7%) of the hydrochloride of 1-methyl-2-benzoylhydroxymethylbenzimidazole. The product crystallizes from aqueous alcohol (1:4) or dilute hydrochloric acid in the form of long, snow-white needles with m.p. 195-197°. On drying it partly loses HCl.

0.0867 g substance: 0.0328 g AgCl. 0.1007 g substance: 0.0446 g AgCl. Found %: Cl 11.08, 10.96. $C_{16}H_{15}O_2N_2Cl$. Calculated %: Cl 11.71.

The base is obtained by treating the hydrochloride with ammonia. After crystallization from water or gasoline, the rhombic crystals melt at 144-146°. In the cold the compound is readily soluble in benzene, alcohol and acetone;

soluble when hot in water and gasoline.

0.0915 g substance: 8.5 ml N_2 (22°, 762 mm). 0.1062 g substance: 9.9 ml N_2 (24°, 762 mm).
Found %: N 10.78, 10.74. $C_{16}H_{16}O_2N_2$. Calculated %: N 10.52.

SUMMARY

1. Acetylation and benzoylation of 2-hydroxy methylbenzimidazole proceed in the first instance at the hydroxyl group of the compound ; subsequently disubsituted derivatives are formed in which the second radical of the organic acid is linked to one of the nitrogen atoms of the heterocycle. The nitrogen-methylated derivative – 1-methyl-2-hydroxymethylbenzimidazole – is only able to yield monoacyl derivatives in which the acyl radical enters at the hydroxyl group.

2. The methoiodide of 1-methyl-2-hydroxymethylbenzimidazole is capable of acetylation at the hydroxy group, but benzoylation cannot be effected.

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SYNTHESES WITH THE AID OF ACRYLONITRILE

XX. CYANOETHYLATION OF ESTERS OF α-AMINO ACIDS

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The cyanoethylation of many types of organic compounds [1] has been studied, but that of amino acids has hardly been studied. Only in recent years have papers been published on the cyanoethylation of α- amino acids [2,3,4,5]. Considering that cyanoethylated derivatives of amino acids are of great interest, we turned our attention to their formation.

In the present communication we set forth the results of our experiments on the cynoethylation of esters of α-amino acids and their hydrochlorides. Depending on the conditions, the reaction products are N-mono- and N,N-dicyanoethylated esters

$$C_2H_5O_2C-CH_2-NH_2 \xrightarrow{CH_2=CH-CN} C_2H_5O_2C-CH_2-NH-CH_2-CH_2-CN \xrightarrow{CH_2=CH-CN} C_2H_5O_2C-CH_2-N(CH_2-CH_2-CN)_2$$

By suitable choice of conditions we can obtain N-monocyanoethylated derivatives without appreciable contamination with N,N-dicyanoethylated compounds.

The materials which we cyanoethylated were the methyl and ethyl esters of glycine and their hydrochlorides, also the hydrochloride of the ethyl ester of phenylalanine. Cyanoethylation of the esters gave only N-monocyanoethylated derivativesin yields of 55 to 70%. Cyanoethylation of glycine ester hydrochlorides by heating for an hour at 70-75° with three times the amount of acrylonitrile gave N-monocyanoethylated derivatives in yields of 51 to 68%. After 10 hours' heating, N,N-dicyanoethylated esters of glycine were isolated in addition to the N-monoderivatives. Cyanoethylation of phenylalanine ethyl ester hydrochloride gave, regardless of the duration of heating, only the N-monocyanoethylated derivative in 78% yield.

The most important side reaction appears to be the formation of cyclic anhydrides, since the process is conducted in presence of alkalies or bases. Moreover the yields of N-cyanoethylated derivatives in the case of the easily cyclized methyl esters of glycine were always lower than in experiments with ethyl esters of glycine and with the hydrochlorides of the ethyl esters of glycine and phenylalanine.

The action of acrylonitrile on N-monocyanoethylated derivatives both without a catalyst and in presence of catalysts (NaOH, triethylamine), but in an anhydrous medium, didnot lead to formation of dicyanoethylated derivatives. But heating of esters of N-monocyanoethylated glycine in water with excess of acrylonitrile for 10 hours at 70-75° leads to preparation of dicyanoethylated derivatives in a yield of about 36%.

Esters of cyanoethylated amino acids are colorless liquids (some of them could be made to crystallize); they distil in vacuum and decompose when distilled not in vacuum. They give a negative ninhydrin reaction.

When treated with an ethereal solution of hydrogen chloride, they form the corresponding hydrochlorides; with an alcoholic solution of ammonia they give the corresponding amides of N-cyanoethylated amino acids. The hydrochlorides of the esters and the amides of cyanoethylated amino acids are crystalline substances.

EXPERIMENTAL

1. Methyl Ester of N Monocyanoethylaminoacetic Acid. $CH_3O_2C-CH_2-NH-CH_2-CH_2-CN$

a) to 5 g (0.056 mole) freshly distilled methyl glycinate in absolute ether is added 6 g (0.112 mole) acrylonitrile. The mixture is left for 3 days and then boiled under a reflux condenser for 5 hours. A considerable amount of diketopiperazine is precipitated during this treatment. After separating the precipitate and distilling off the ether, the reaction product is vacuum-distilled: b.p. 142-143° at 12 mm. Yield 4.4 g, i.e. 55.2% Colorless liquid, soluble in water, ethanol and ether, n_D^{20} 1.4530, d_4^{20} 1.0983; MR$_D$ 34.99; calculated 34.98.

7.608 mg substance: 14.277 mg CO_2; 4.912 mg H_2O. 7.523 mg substance: 14.145 mg CO_2; 4.860 mg sub- H_2O. 77.1 mg substance: 10.91 ml 0.1 N H_2SO_4. 75.3 mg substance: 10.6 ml 0.1 N H_2SO_4. Found %: C C 51.21, 51 31; H 7.22, 7.22; N 19.80, 19.71. $C_6H_{10}O_2N_2$. Calculated %: C 50.69, H 7.09, N 19.77.

The hydrochloride was prepared by adding an ethereal solution of HCl. Crystals (from ethanol), m.p. 137°, readily soluble in water and boiling ethanol. Found %: Cl 19.53, 19.79. $C_6H_{11}O_2N_2Cl$. Calculated %: Cl 19.85.

b) Into a three-necked, round-bottomed flask, fitted with mechanical stirrer, a reflux condenser and dropping funnel was introduced 10 g (0.08 mole) methylglycinate hydrochloride. Addition was made of 5 ml water, 12.6 g (0.24 mole) acrylonitrile and (with stirring for 15 minutes at 50°) 4.4 g (0.08 mole) KOH dissolved in 15 ml water. The mixture was heated for an hour at 70-75°. The reaction product was separated from the aqueous layer and the latter was extracted 3-4 times with ether. The ethereal extracts, together with the upper layer, were dried with sodium sulfate. After driving off the ether and the excess of acrylonitrile, the methyl ester of N-monocyanoethylglycine was distilled in vacuum. B.p. 142-143° at 12 mm. Yield 5.8 g (51.3%).

2. Methyl Ester of N, N-Dicyanoethylglycine. $CH_3O_2C-CH_2-N(CH_2-CH_2-CN)_2$

The reaction was conducted as in experiment 1 b. The amounts of reactants were the same. The mixture was heated for 10 hours at 70-75°. The methyl ester of N-monocyanoethylglycine boils at 142-143° at 12 mm. Yield 2 g (17.8%). The boiling point of the methyl ester of N, N-dicyanoethylglycine is 218-219° at 12 mm. Yield 3.4 g (21.9%). Colorless oil, crystallizing when cooled with ice. M.p. 59.5-60° (from water); readily soluble in ethanol, ether and hot water; less easily in cold water.

7.355 mg substance: 14.876 mg CO_2; 4.413 mg H_2O. 6.575 mg substance: 13.318 mg CO_2; 3.970 mg H_2O. 73.9 mg substance: 11.33 ml 0.1 N, H_2SO_4. 71.1 mg substance: 10.91 ml 0.1 N H_2SO_4. Found %: C 55.20, 55.28; H 6.71, 6.76; N 21.46, 21.47. $C_9H_{12}O_2N_3$. Calculated %: C 55.36; H 6.71; N 21.52.

The hydrochloride forms crystals with m.p. 121-121.5° (from ethanol); readily soluble in water and boiling ethanol. Found %: Cl 15.25, 15.17. $C_9H_{13}O_2N_3Cl$. Calculated %: Cl 15.30.

3. Ethyl Ester of N-Monocyanoethylglycine. $C_2H_5O_2C-CH_2-NH-CH_2-CH_2-CN$

a) The reaction was performed as in experiment 1a. To 5 g (0.048 mole) ethyl glycinate is added 5.1 g (0.096 mole) acrylonitrile. The boiling point of the ethyl ester of N-monocyanoethylglycine is 148-149° at 12 mm. Yield 5.3 g (70.5%). Colorless liquid, soluble in water, ethanol and ether. n_D^{20} 1.4498; d_4^{20} 1.0615; MR_D 39.52; Calculated: 39.60.

6.820 mg substance: 13.390 mg CO_2; 4.810 mg H_2O. 5.785 mg substance: 11.385 mg CO_2; 4.132 mg H_2O. 106.2 mg substance: 13.8 ml 0.1 N H_2SO_4. 109.9 mg substance: 14.25 ml 0.1 N H_2SO_4. Found %: C 53.58, 53.71; H 7.89, 7.99; N 18.19, 18.15. $C_7H_{12}O_2N_2$. Calculated %: C 53.82; H 7.74, N 17.93.

The hydrochloride forms crystals with m.p. 113° (from ethanol); readily soluble in water and boiling ethanol.

Found %: Cl 18.04, 18.35. $C_7H_{13}O_2N_2Cl$. Calculated %: Cl 18.40.

N-Monocyanoethylglycinamide was prepared by treating 3 g of ethyl ester of N-monocyanoethylglycine with 45 ml of methanol solution of ammonia saturated at 0°. The solution was kept for 24 hours after which the methanol and excess ammonia were removed by evaporation in vacuum. The solid residue was recrystallized. Platelets (from ethanol), m.p. 46-47°. Yield 1.9 g (79.2%). Soluble in water, ethanol and chloroform; insoluble in ether.

7.690 mg substance: 13.350 mg CO_2; 4.890 mg H_2O. 8.690 mg substance: 15.100 mg CO_2; 5.600 mg H_2O. 46.6 mg substance: 11.0 ml 0.1 N H_2SO_4. 51.6 mg substance: 12.16 ml 0.1 N H_2SO_4. Found %: C 47.37, 47.39; H 7.12, 7.21. N 33.05, 32.98. $C_5H_9ON_3$. Calculated %: C 47.23; H 7.13; N 33.05.

b) The reaction was performed as in experiment 1 b. To 10 g (0.07 mole) ethyl glycinate hydrochloride were added 5 ml water, 11.4 g (0.21 mole) acrylonitrile and 4 g (0.07 mole) KOH dissolved in 15 ml water, and the mixture was heated for an hour at 70-75°. The ethyl ester of N-monocyanoethylglycine boils at 148-149° at 12 mm. Yield 7.6 g (67.8%).

4. Ethyl Ester of N, N-Dicyanoethylglycine $C_2H_5O_2C-CH_2-N(CH_2-CH_2-CN)_2$

The reaction was performed as in experiment 1b.

The quantities of reactants were the same. The mixture was heated for 10 hours at 70-75°. The ethyl ester of N-monocyanoethylglycine boils at 148-149° at 12 mm. Yield 2.6 g (23.2%). The boiling point of the ethyl ester of N, N-dicyanoethylglycine is 221-222° at 12 mm. Yield 4.4 g (29.0%). Colorless oil which crystallizes when cooled with ice, but again changes into oil at room temperature. Readily soluble in ethanol, ether,

and hot water; less readily soluble in cold water.

8.080 mg substance: 17.020 mg CO_2; 5.385 mg H_2O. 6.235 mg substance: 13.090 mg CO_2; 4.095 mg H_2O. 67.5 mg substance: 9.75 ml 0.1 N H_2SO_4. 55.7 mg substance: 8.05 ml 0.1 N H_2SO_4. Found %: C 57.48, 57.30; H 7.46, 7.35; N 20.22, 20.23. $C_{10}H_{15}O_2N_3$. Calculated %: C57.39; H 7.22; N 20.08.

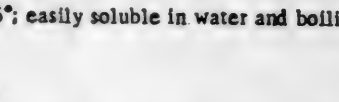
The hydrochloride forms crystals (from ethanol) with m.p. 121-121.5°; easily soluble in water and boiling ethanol.

Found %: Cl 14.23, 14.38. $C_{10}H_{16}O_2N_3Cl$. Calculated %: Cl 14.43.

N,N-Dicyanoethylglycinamide was prepared as in experiment 3a by treating 4 g ethyl N,N-dicyanoethylglycinate with 60 ml of methanol solution of ammonia. Platelets (from ethanol) with m.p. 95.5°. Yield 3 g (81.4%). Soluble in water and ethanol; insoluble in ether.

8.100 mg substance: 15.870 mg CO_2; 4.910 mg H_2O. 6.320 mg substance: 12.430 mg CO_2; 3.910 mg H_2O. 48.8 mg substance: 11.01 ml 0.1 N H_2SO_4. 52.6 mg substance: 11.64 ml 0.1 N H_2SO_4. Found %: C 53.47, 53.67; H 6.78, 6.92; N 30.94, 30.97. $C_8H_{12}ON_4$. Calculated %: C 53.31; H 6.71; N 31.09.

5. Ethyl Ester of N-Monocyanoethyl-β-phenylalanine



The reaction was performed as in experiment 1 b. To 10 g (0.04 mole) phenylalanine ethyl ester hydrochloride was added 5 ml water, 6.8 g (0.12 mole) acrylonitrile and 2.4 g (0.04 mole) KOH dissolved in 15 ml water, and the mixture was heated for 5 hours at 70-75°. The boiling point of the ethyl ester of N-monocyanoethylphenylalanine is 191-192° at 8 mm. Yield 8.4 g (78.5%); Colorless liquid, soluble in ethanol and ether, insoluble in water.

n_D^{24} 1.5110; d_4^{20} 1.0763; MR_C Found 63.77; Calculated 63.22.

3.085 mg substance: 7.736 mg CO_2; 2.080 mg H_2O. 4.965 mg substance: 12.400 mg CO_2; 3.294 mg H_2O. 134.1 mg substance: 11.0 ml 0.1 N H_2SO_4. 111.6 mg substance: 9.03 ml 0.1 N H_2SO_4. Found %: C68.17, 68.16; H 7.54, 7.42; N 11.48, 11.33. $C_{14}H_{18}O_2N_2$. Calculated %: C 68.27; H7.36; N 11.37.

The hydrochloride forms platelets (from ethanol) with m.p. 166°; readily soluble in water and boiling ethanol.

Found %: Cl 12. 56, 12.44. $C_{14}H_{19}O_2N_2Cl$. Calculated %: Cl 12.54.

The amide of N-monocyanoethylphenylalanine was prepared as in experiment 3a by standing 2 g ethyl ester of N-monocyanoethylphenylalanine with 50 ml methanol solution of ammonia for 5 days. Lustrous platelets (from ethanol) with m.p. 108.5°. Yield 1.4 g (82.3%). Soluble in water and ethanol.

8.125 mg substance: 19.618 mg CO_2; 5.000 mg H_2O. 5.597 mg substance: 13.518 mg CO_2; 3.515 mg H_2O. 68.3 mg substance: 9.4 ml 0.1 N H_2SO_4 64.2 mg substance: 8.8 ml 0.1 N H_2SO_4. Found %: C C 65.69, 65.91; H 6.89, 7.03; N 19.27, 19.19. $C_{12}H_{15}ON_3$ Calculated %: C 66.33, H 6.96; N 19.34.

SUMMARY

The reaction of acrylonitrile with esters of amino acids and their hydrochlorides was studied.

The following were prepared and characterized for the first time: the methyl and ethyl esters of N-mono- and N,N-dicyanoethyl-glycine and the ethyl ester of N-monocyanoethyl-phenylalanine, also their hydrochlorides.

The action of ammonia on the esters of N-cyanoethyl-amino acids was studied. For the first time prepared and characterized were the amides of N-mono- and N,N-dicyanoethyl-phenylalanine.

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THE REACTION OF ARYL SULFAMIDES WITH AMINES. II.

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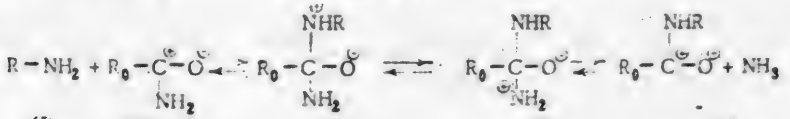
In the preceding communication [1] it was pointed out that amines which form amides of aromatic sulfonic acids are displaced in certain conditions by primary aromatic amines. If the primary amine is replaced by a tertiary one, for example dimethylaniline, then the latter in these cases splits off one methyl group, and the formed monomethylaniline displaces the radical of the primary amine from the sulfamide group.

The process of displacement may also be regarded as an acylation of the primary or secondary amine by sulfamides.

In connection with our studies of aminolysis of sulfamides it seemed of interest to apply the catalytic action of hydrogen chloride [1] to the rupture of the isothiazole ring of saccharin not only at the C–N bond but also at the S–N sulfamide linkage. The ammonia released in this reaction, by combining with the hydrogen chloride, should form ammonium chloride which in the given conditions should be removed from the sphere of reaction as a solid phase.

On heating saccharin with aniline hydrochloride in a sealed tube at 200° for 15 minutes, however, the main reaction proved to be dehydration, leading to formation of phenylpseudosaccharin

In regard to the mechanism of the process in question, attention may be directed to the views of B. A. Porai-Koshits [2,3] on the acylation of amines which, in our opinion, can be extended to a series of other reactions and, in particular, to the acylation of amines by carboxylic acid amides:



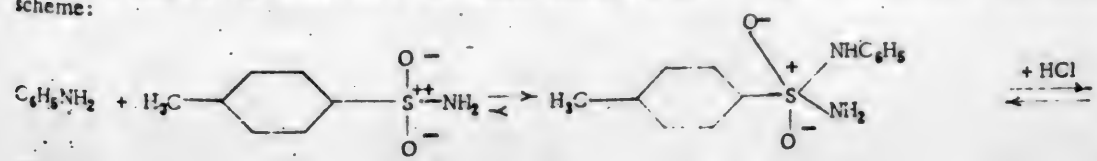
(I) (II) (III) (IV) (V)

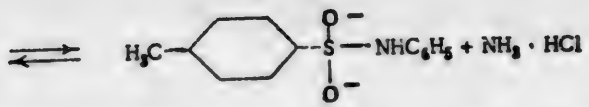
According to this scheme, only the free amine enters into reaction; the intermediate product (III) is formed by entry of the unshared electron pair of nitrogen (I) into the electron-deficient system of the carbon atom of the carbonyl group of the amide which reacts in the polarized form (II). Stabilization of the intermediate product is effected as a result of separation of a molecule of the other amine, an important part in this process being played by the degree of basicity of the competing amines. The catalytic activity of hydrogen ions in this reaction must be associated with the considerable polarization of the double bond of the carbonyl group due to addition of a proton to the oxygen and to formation of a cation with an electron deficiency at the carbon atom:

Smith and Adkins [4] have also drawn attention to the possibility of formation of an intermediate addition product.

To a certain extent, such a reaction mechanism ought to be applicable to the process of acylation of amines by sulfonic acid amides [5].

For example, the interaction of p-toluenesulfanilide with aniline might be represented by the following scheme:

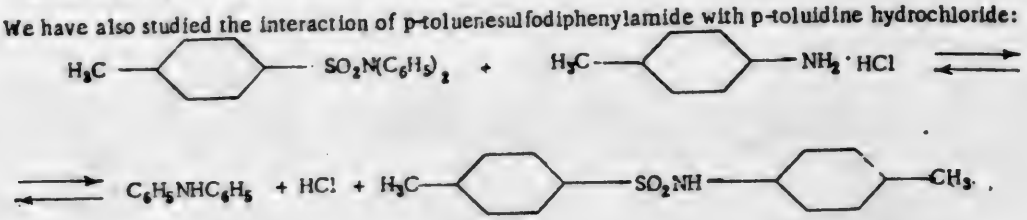




In that event, the center of addition of the amine is the electronophilic atom of sulfur and not the carbon atom in carbamides.

As was indicated previously [1], the phase equilibria factors exert a considerable influence on the course of the investigated exchange reaction. Supplementary date on this matter are presented in the experimental part.

We have also studied the interaction of p-toluenesulfodiphenylamide with p-toluidine hydrochloride:



where the release of hydrogen chloride in the gas phase facilitated the course of the reaction from left to right.

EXPERIMENTAL

1. Interaction of saccharin with aniline hydrochloride. A thoroughly pulverized mixture of 0.92 g saccharin and 0.6 g aniline hydrochloride was heated in a sealed tube at 200° for 25 minutes. The cooled and pulverized mass was extracted with hot water; on cooling, yellowish crystals came down, m.p. 222°; after crystallization from alcohol the m.p. was 225°; the m.p. of a mixture with saccharin was also 225°. The residue dissolved completely in dilute alkali. Aniline did not separate when the solution was heated. The solution was treated with hydrochloric acid until weakly alkaline and was decolorized with carbon. Acidification of the filtrate yielded 0.72 g phenylpseudosaccharin with m.p. 315° [6].

2. Interaction of N,N'-di-p-toluenesulfonylbenzidine [7] with benzidine dihydrochloride. Molar ratio 1.4:1; temp. 320-340°; duration 5 minutes. There was no exchange reaction.

3. Interaction of p-toluenesulfanilide with benzidine dihydrochloride. Molar ratio 2:1; temp. 190°; duration 35 minutes. No exchange reaction took place.

4. Interaction of N,N'-di-p-toluenesulfonylbenzidine with aniline hydrochloride. A well pulverized mixture of 0.8 g di-p-toluenesulfonylbenzidine and 0.6 g aniline hydrochloride was heated for 15 minutes in a sealed tube at 225-230°. After the tube had been cooled and opened, it was crushed and pulverized together with the contents and extracted several times with 1:1 hydrochloric acid. Benzidine was precipitated from the hydrochloric acid extracts on treatment with alkali; no precipitate came down when the alkaline solution was acidified. The benzidine was converted into the sulfate which was titrated with NaOH solution in presence of phenolphthalein. Yield 0.29 g (96.6% of the theoretical).

The precipitate after extraction was dissolved in 16 ml 10% NaOH solution. After filtration and decolorization with charcoal, fractional precipitation was effected by acidification. Fractions melting at 101-103° were obtained, corresponding to p-toluenesulfamide. Yield 0.74 g (93% of the theoretical).

5. Transformation of mono-p-toluenesulfonylbenzidine hydrochloride [8] by heat. The hydrochloride (0.5 g) was heated at 250° for 15 minutes. The pulverized melt was extracted with 1:1 hydrochloric acid while heating on the water bath. Treatment of the extracts with alkali brought down benzidine. The amount of the latter was determined as above. Yield 0.087 g (63% of the theoretical).

The alkaline filtrate after precipitation of benzidine base was treated with hydrochloric acid until weakly alkaline, decolorized with carbon and finally acidified with acetic acid. A white precipitate of the unchanged mono-derivative came down, m.p. 164°. A mixed test also gave m.p. 164°.

The residue of the melt was pulverized and reprecipitated with hydrochloric acid from a large volume of dilute sodium hydroxide solution (decolorization with carbon). p-Toluenesulfonylbenzidine with m.p. 241° was precipitated; mixed m.p. also 241°.

6. Interaction of p-toluenesulfodiphenylamide [9] with p-toluidine hydrochloride. Into a solution of 0.56 g p-toluidine and 1.3 g p-toluenesulfodiphenylamide in 5 ml ether was passed a stream of dry hydrogen chloride

until saturated. After driving off the ether, the mixture was heated at 185° for 30 minutes. The mass was washed with dilute hydrochloric acid and with hot water. From the aqueous extracts were precipitated colorless platelets of diphenylamine (m.p. 54°; mixed melting point also 54°). The alkaline extracts were gradually acidified with with 1 N hydrochloric acid and left overnight; p-toluenesulfo-p-toluidide came down and after crystallization from alcohol melted at 118° [10].

SUMMARY

1. The main product of reaction of saccharin with aniline hydrochloride is phenylpseudosaccharin.
2. New cases of interaction between arylsulfamides and hydrochlorides of amines were investigated.
3. Suggestions about the mechanism of the investigation reaction were advanced.

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